

Evaluating Design Parameters for Breakthrough Curve Analysis and Kinetics of Fixed Bed Columns for Cu(II) Cations Using Lignocellulosic Wastes

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A continuous adsorption study for removal of Cu(II) cations from wastewater using a fixed-bed column was conducted. A granular carbonaceous activated adsorbent produced by carbonization of the outer rind, or exocarp, of mangostene fruit shell was used for column packing. The effects of feed flow rate, influent cation concentration, and bed depth on the breakthrough curve were investigated at pH 5.5. Experimental analysis confirmed that the breakthrough curves were dependent on flow rate, initial concentration of Cu(II) cations, and bed height related to the amount of activated carbon used for column packing. Thomas, Yoon–Nelson, and Adams–Bohart models were applied to analyze the breakthrough curves at different conditions. Linear regression analysis of experimental data demonstrated that Thomas and Yoon–Nelson models were appropriate to explain the breakthrough curve, while the Adams–Bohart model was only applicable to predict the initial part of the dynamic process. It was concluded that the column packed with fruit rind based activated carbon can be used to treat Cu(II)-enriched wastewater.

Keywords: Fixed-bed; Thomas model; Yoon–Nelson models; Adams–Bohart model; Breakthrough Curve

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INTRODUCTION

The transformation of readily available renewable residues of lignocellulosic biomass to valuable chemicals has been recognized as an efficient approach for alleviation of increasing environmental pollution, the energy crisis, and climate change (Wu *et al.* 2012; Chao *et al.* 2014; Chowdhury *et al.* 2014). One of the biggest challenges is to overcome the recalcitrance of lignocellulosic biomass and convert it to carbonaceous adsorbent materials with desirable properties. Lignocellulosic biomass wastes are usually porous and lightweight, having carboxylic and hydroxyl functional groups attached to their surfaces (Chowdhury *et al.* 2013). But applicability of those raw precursors in their original condition is restricted up to a certain extent owing to their inadequate surface areas, pore size distributions, and leaching of organic substances into aqueous solution. The effective resolution to this challenge basically depends upon the pyrolysis of biomass residues with careful optimization of preparation variables including temperature, time, and impregnating agent with proper ratio. This would comprehensively modify the surface area, pore volume, and pore size distribution, including the percentages of micro- and mesopores inside the carbon matrix. Controlled oxidation or activation practices during the preparation of activated carbon would enhance carboxylate and phenolic groups, which can act as necessary binding groups for divalent cations. Commercially

available activated carbons are generally obtained from coal, lignite, and peat. Thus its application is still expensive and unjustified for treating aqueous effluents (Sourja *et al.* 2005; Ahmad *et al.* 2010). Therefore, in recent years, the research trend has shifted towards production of activated carbon from abundantly available, renewable resources of lignocellulosic biomass. Numerous studies have been carried out to prepare carbon from paper mill sludge (Khalili *et al.* 2000), digested sewage sludge, coconut husk (Tay *et al.* 2001), phoenix tree leaf powder (Han *et al.* 2009), cassava peel (Sudaryanto *et al.* 2006), palm fronds (Salman and Hameed 2010), palm shell (Adinata *et al.* 2007; Sumathi *et al.* 2009; Arami-Niya *et al.* 2012), Luscar char (Azargohar and Dalai 2005), olive seed waste (Stavropoulos and Zabaniotou 2005), oil palm fiber (Hameed *et al.* 2008), rubber wood sawdust (Srinivasakannan and Bakar 2004), turkish lignite (Karacan *et al.* 2007), bamboo waste (Ahmad *et al.* 2010), waste rapeseed (Tofan *et al.* 2011), oil palm ash (Chowdhury *et al.* 2011a,c), and rattan sawdust (Ahmad *et al.* 2009).

The presence of metallic cations in the aquatic environment and their accumulation in the food chain is of great concern at present. Even at lower concentrations, metallic cations are highly toxic, non-biodegradable, and can assimilate inside the living tissues of an organism, causing adverse effects (Malkoc and Nuhoglu 2006). Acute exposure to copper can cause vomiting, hematemesis (vomiting of blood), hypotension (low blood pressure), melena (black "tarry" feces), coma, jaundice (yellowish pigmentation of the skin), and gastrointestinal distress (Klassen 1995). Copper cations can be discharged in aqueous effluents from various industries including mining, brass manufacturing, smelting, and electroplating (Chen and Wang 2000). Currently, different types of treatment processes including precipitation, oxidation-reduction, membrane filtration, osmosis, ion exchange, and ozonation techniques are widely used. These processes have inherent limitations such as high cost, formation of perilous sludge, and intensive energy consumption (Malkoc and Nuhoglu 2006). Adsorption onto pretreated biomass or carbonaceous materials derived from lignocellulosic residues has been found to be superior for wastewater treatment compared to other physiochemical techniques.

Batch adsorption is usually carried out to measure the effectiveness of adsorption for eliminating specific adsorbates as well as to estimate the maximum adsorption capacity. Fixed-bed column adsorption is preferred for industrial scale application, because it can be scaled-up easily from a laboratory process (Ahmad and Hameed 2010). A continuous fixed bed column does not run under equilibrium conditions, and the effect of process variables at any cross-sectional area of the column affects the overall flow behavior and operating limit of the column. The performance and mass transfer aspects of the column become unusual beyond a particular length to diameter ratio of the column. Adsorption in fixed-bed columns using activated carbon has been extensively used in industrial processes for the removal of organic contaminants from aqueous effluents, but its application for metal waste treatment is relatively less studied (Chen and Wang 2004).

Mangostene (*Mangostana garcinia*) fruits are mainly cultivated in tropical regions. They grow abundantly in Thailand, Malaysia, Indonesia, Brazil, Panama, and Hawaii. After consumption of the fruits, the peels or exocarp of the fruits are thrown without any potential application. Thus from an environmental perspective, safe discarding of these lignocellulosic wastes is immensely important. In this research, the single-component sorption of copper (II) cations using a fixed bed column packed with granular activated carbon derived from mangostene exocarp has been studied. The effect of system variables—including metal ion concentration, flow rate, and bed height—was examined. The shape of the breakthrough curve has been analyzed to correlate the solid-phase loading

and exhaustion time of the filter bed. Column kinetics has been studied by using Thomas, Yoon-Nelson, and Adams-Bohart models. Column regeneration and recycling have been conducted through four cycles to ascertain the practical applicability of the prepared adsorbent for large scale industrial application.

EXPERIMENTAL

The carbon used here for column packing was prepared by two steps using the physiochemical activation method described in our previous work (Chowdhury *et al.* 2012b). At first stage, carbonization of the raw peel was conducted at low temperature. It was further activated at high temperature after impregnating with a base catalyst of potassium hydroxide (KOH).

Preparation of Activated Adsorbent

The dried peels were cut into 2 to 3 mm sized pieces and washed carefully to remove dirt and inorganic substances on their surfaces. They were dried in an oven at a temperature of 105 °C for 24 h to remove all moisture. Fifty grams of dried fruit peel was carbonized by using a tubular reactor in which metal mesh is placed at the bottom to prevent sample loss. At the carbonization stage, purified nitrogen gas was supplied inside the sample to ensure complete evacuation of oxygen to create an inert atmosphere inside the reactor. The carbonization nitrogen flow rate and heating rate were maintained at 150 cm³/min and 10 °C/min, respectively. The temperature was increased from room temperature to 400 °C and kept constant for 2 h.

The product thus obtained was cooled and mixed with KOH pellets, maintaining the ratio of 1:1. The mixture was dried in an oven and finally activated at 750 °C for 2 h by using carbon dioxide gas flow. The tubular reactor containing the sample was placed inside the furnace by a support. A K-type thermocouple that can withstand a maximum temperature limit of 1000 °C was placed inside the sample. Another similar thermocouple was positioned outside the reactor to measure the temperature of the furnace. The activated carbon thus obtained was washed, dried, and stored carefully for the subsequent stage of column packing for fixed bed sorption.

Preparation of the Single Solute System

The single solute system of Cu(II) cations having a concentration of 1000 mg/L was prepared by dissolving the required amount of CuCl₂·2H₂O salt. The test solution, having a concentration range of 50 mg/L, 70 mg/L, and 100 mg/L, was prepared by fresh dilution of the stock solution.

Fixed Bed Adsorption Study

Continuous flow adsorption studies were conducted by using a Pyrex glass column with an internal diameter of 4.5 cm with height 30 cm. A stainless steel sieve was positioned at the bottom of the column with a layer of glass wool placed over it. The requisite amount of activated adsorbent was packed in the column to obtain the desired bed height. Another layer of glass wool was placed over the adsorbent surface. Copper (II) solution of a certain concentration at pH 5.5 was pumped upward at the desired flow rate by using a peristaltic pump (Model Masterfiex, Cole-Parmer Instrument Co., US). At the

outlet of the column, the treated water sample was collected at regular time intervals, and residual concentration was measured.

Column Regeneration Studies

The performance of a column can be evaluated by regeneration and recycling of activated adsorbent. In this context, regeneration of the carbon was carried out by using 1 M nitric acid (HNO_3) solution at a flow rate of 3 mL/min for 16 h. This would provide sufficient exchangeable H^+ ions to desorb copper cations completely (Chowdhury *et al.* 2012). After each cycle, the adsorbent was washed with hot distilled water, dried, and then packed inside the column for further studies. The regeneration efficiency was calculated for the bed height (4.5 cm), flow rate (1 mL/min), and initial concentration of 100 mg/L by using the following equation (Eq. 1),

$$\text{Regeneration Efficiency \%} = (q_{\text{reg}}/q_{\text{org}}) \times 100 \quad (1)$$

where q_{reg} is the adsorptive capacity of the regenerated column and q_{org} is the sorption capacity (mg/g) of the adsorbent after each cycle.

The breakthrough time (t_b), complete exhaustion time (t_e), and bed capacity for different conditions were determined. In this study, the column sorption capacity for removal of adsorbate at 50% breakthrough (mg/g) was estimated using the following Eq. 2 (Treybal 1980; Baral *et al.* 2009):

$$\begin{aligned} &\text{Adsorption column capacity at 50\% breakthrough, } q_{\text{org}} \\ &= [\text{Breakthrough time, } t_{50} \text{ (at 50\%)} \text{ (min)} \times \text{flow rate, } Q \text{ (mL/min)} \times \\ &\text{feed concentration, } C_0 \text{ (mg/L)}] / \text{mass of adsorbent in bed, } m \text{ (g)} \end{aligned} \quad (2)$$

Empty bed contact time (EBCT) or standard contact time was calculated by using Eq. 3 (Bharathi *et al.* 2011):

$$\text{EBCT} = \text{Bed Volume, BV} / \text{Flow rate, } Q \quad (3)$$

RESULTS AND DISCUSSION

Breakthrough Curve Analysis

In static mode batch adsorption studies, the same solution remains in contact with a certain quantity of the adsorbent. The adsorption process continues until equilibrium is established between the solute present in the liquid phase and the solute sorbed per unit weight of the sorbent. In fixed bed adsorption, influent solution continuously enters and leaves the column packed with sorbent. Consequently, complete equilibrium is never established at any stage between the solute present in the solution and the amount adsorbed. It follows that equilibrium must be continuously established within the column as the sorbent encounters new concentrations of solute. That is why an equilibrium system in column mode/fixed bed is called a dynamic equilibrium of sorption (Chowdhury 2013). The performance of continuous adsorption by using a fixed bed packed with granular activated carbon (GAC) is explained in terms of a breakthrough curve. The time required for breakthrough and the shape of the breakthrough curves are very important characteristics for evaluating the dynamic response of an adsorption system (Malkoc *et al.* 2006). The

loading behavior of Cu(II) cations in a fixed bed is expressed in term of C_t/C_0 with respect to time for a given bed height, flow rate, and initial metal ion concentration which consequently gives a breakthrough curve. Figure 1 shows different steps in the column sorption process, whereas Fig. 4 illustrates the breakthrough curve as a function of contact time.

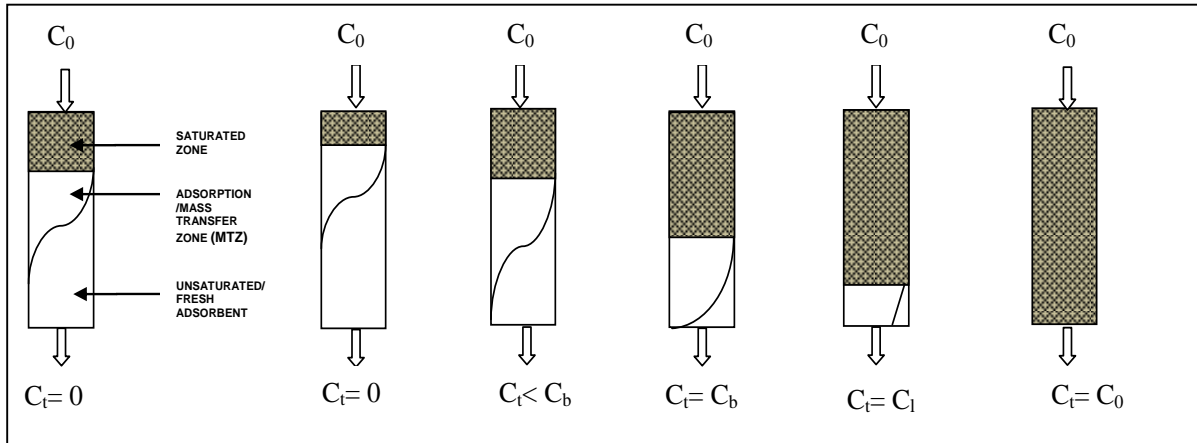


Fig. 1. Schematic representation of saturated, mass transfer or adsorption, and unsaturated or fresh adsorbent zones in fixed bed column adsorption

In a fixed bed column, the flow of polluted water creates a wave front through the adsorbent bed (Fig. 1). The wave front covering the area near the inlet side is known as the mass transfer zone (MTZ). The sorption process takes place in the mass transfer zone.

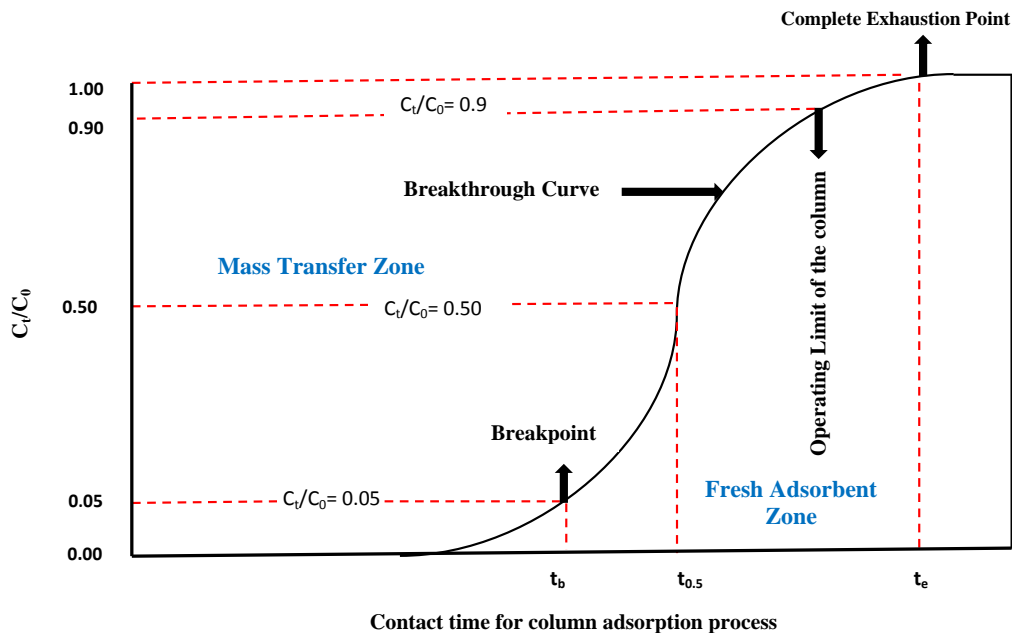


Fig. 2. Breakthrough curve characteristics in the fixed bed column adsorption process with respect to time

As the activated adsorbent becomes exhausted over time, the mass transfer zone moves forward across the adsorbent bed. When the mass transfer zone travels forward, it leaves behind the portion of the adsorbent bed that is saturated by the contaminants. Thus, the edge of the mass transfer zone reaches the end of the column and breakthrough occurs. The graphical representation for the movement of the mass transfer zone (MTZ) through the column is called a breakthrough curve. However, the breakthrough point is usually defined as the point when the ratio between influent concentration, C_0 (mg/L) and outlet concentration, C_t (mg/L) becomes 0.05 to 0.90, as illustrated by Fig. 2. The adsorbent from the column is usually replaced when the ratio between the inlet and outlet concentration, C_t/C_0 becomes 0.50 at time $t_{0.5}$ (min) in the case of industrial scale application, *i.e.*, 50% breakthrough of the column. The column sorption capacity is calculated at this point (Baral *et al.* 2009). After the 50% breakthrough point, the column can still operate until the ratio C_t/C_0 becomes 0.90. This point is termed as the operating limit of the column, and at this point the outlet concentration is denoted as C_1 (Fig. 1). The column will be completely exhausted when the pre-determined inlet concentration is almost equal to the outlet concentration, *i.e.*, $C_0 \approx C_t$ or C_1 (Fig. 1) at time t_e (min).

Effect of Influent Concentration

The effect of influent concentration on the breakthrough curve was studied by varying the concentrations of 50, 70, and 100 mg/L. In this case, the bed height of 4.5 cm and influent flow rate of 1 mL/min were kept constant. The breakthrough curve obtained for various concentration ranges is illustrated by Fig. 3.

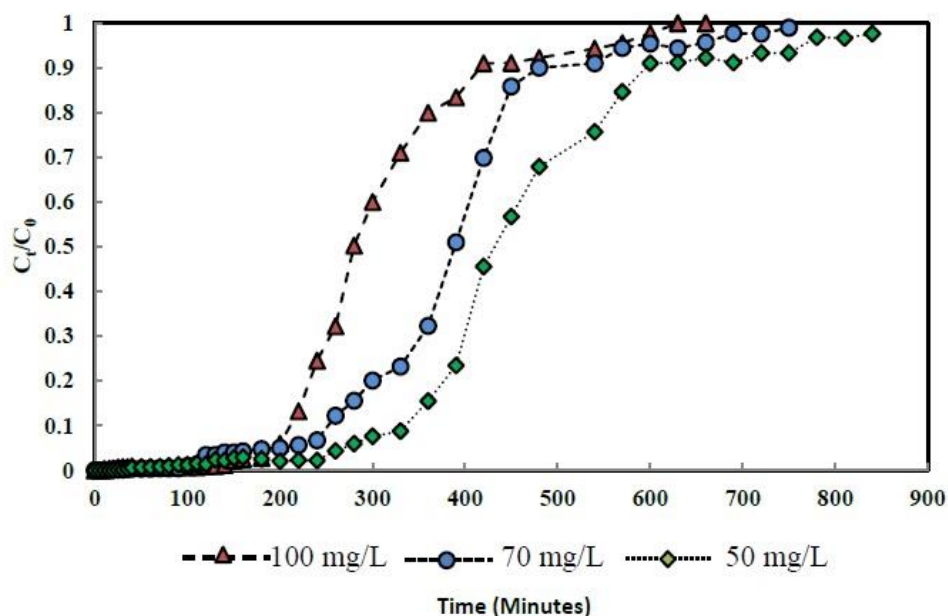


Fig. 3. Breakthrough curves for adsorption of copper (II) cations for different initial concentrations (bed height 4.5 cm, flow rate 1 mL/min, pH 5.5, temperature 30 ± 1 °C)

As the concentration range was increased from 50 mg/L to 100 mg/L, the curve changed from its flatter concave shape to a steep concave shape; the larger the influent concentration is, the steeper the shape of the initial portion of the curve. Nevertheless, it had an S-shaped curve for all the concentrations with a nearly straight line for the preliminary stage of the breakthrough curve. A similar trend was observed for the biosorption of Cr(VI) by the thermally activated weed *Salvinia cucullata* (Baral *et al.*

2009), biosorption of Acid Blue 15 using fresh water *Azolla filiculoides* (Padmesh *et al.* 2006), adsorption of Pb(II) cations onto activated tea waste (Mondal 2009), and immobilized *Pinus sylvestris* sawdust (Taty-Costodes *et al.* 2005).

As can be observed from the plot (Fig. 3), the activated adsorbent bed was exhausted faster at the higher initial concentration of Cu(II) cations. It is observed that the breakthrough point was reached more quickly with the 100 mg/L solution than with the other two concentrations (50 mg/L and 70 mg/L). This phenomenon is expected with increasing influent concentration. For the higher concentration range, the binding sites were occupied rapidly and the column bed was saturated within a short period of time. When the inlet concentration was decreased to 50 mg/L or 70 mg/L, relatively longer contact time was required for the fixed bed to be exhausted. This gave an extended breakthrough curve. The result demonstrated that for the lower concentration range, larger volumes of wastewater solution could be treated for a longer contact period. This is evident due to the slower transportation of adsorbate cations for the lower concentration solution. This results in an overall decrease in the diffusion or mass transfer coefficient (Tan *et al.* 2008).

Effect of Bed Height

Figure 4 shows the breakthrough curve obtained for the adsorption of Cu(II) cations using two different bed heights of 3 and 4.5 cm (3.56 and 4.86 g of activated adsorbent) in a fixed bed column. For this case, influent flow rate (1 mL/min) and inlet concentration of Cu(II) cations (100 mg/L) were kept constant. The breakthrough curve showed comparatively less steep tendencies for higher bed height, reflecting an extended breakthrough time. Maximum equilibrium capacity of the column increased with increasing bed height.

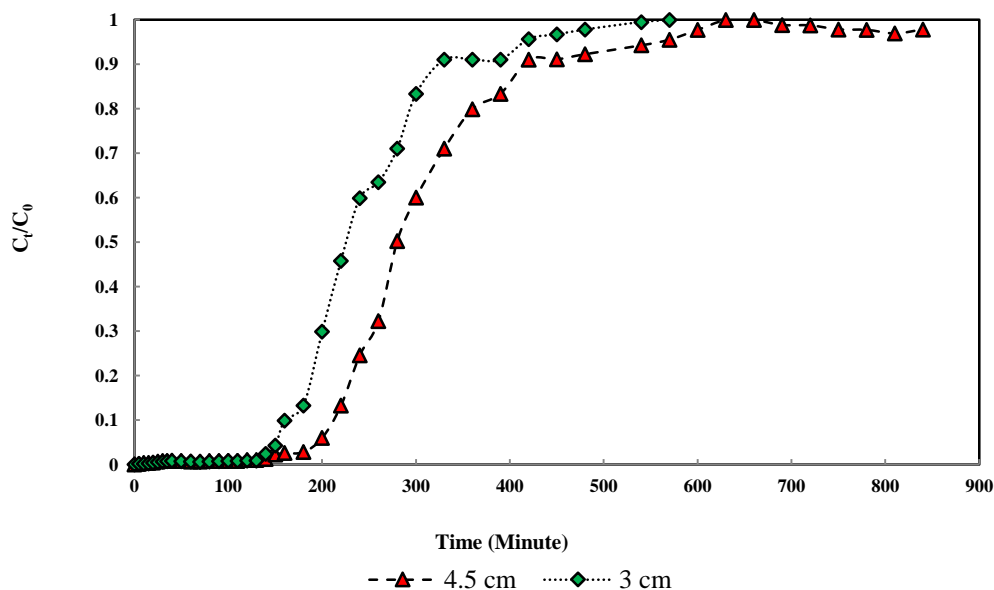


Fig. 4. Breakthrough curves for adsorption of copper (II) cations for different bed height (concentration 100 mg/L, Flow rate 1 mL/min, pH 5.5, temperature 30±1 °C)

As can be seen from the plots, both breakthrough time and exhaustion time were found to increase with increasing bed height. For the higher bed height, more activated adsorbent was used for column packing. Thus, there were more active sites for capturing metallic cations, resulting in greater uptake capacity. As depicted earlier, the mass transfer zone travels from the inlet side of the fixed bed column and moves forward towards the outlet side of the column.

The breakthrough time would be more for the higher bed height using a constant flow rate (1 mL/min) and concentration (100 mg/L). A larger volume of water could be treated by the column using a larger bed height (Tan *et al.* 2008; Ahmad and Hameed 2010). A similar trend was reported for adsorption of Cr(VI) onto immobilized cyanobacterial biosorbents (Kiran and Kaushik 2008) and Cr(VI) on neem sawdust (Vinodhini and Das 2010).

Effect of Influent Flow Rate

The effect of influent flow rate on the adsorption of Cu(II) cations using a fixed bed was investigated by varying the flow rate (1 and 3 mL/min) while keeping the bed height of 4.5 cm and inlet adsorbate concentration of 100 mg/L constant. The breakthrough curves are illustrated by Fig. 5.

It was observed that at a higher flow rate, the column was exhausted earlier. The fixed bed was saturated quickly. For the higher flow rate, the front of the mass transfer zone reached near to the exit of the column quickly (Vinodhini and Das 2010). In the case of lower flow rate, longer contact time is required for exhaustion of the column. For higher flow rate, the curve was steeper resulting in a smaller removal percentage and uptake of the metal.

The sorption parameters are listed in Table 1.

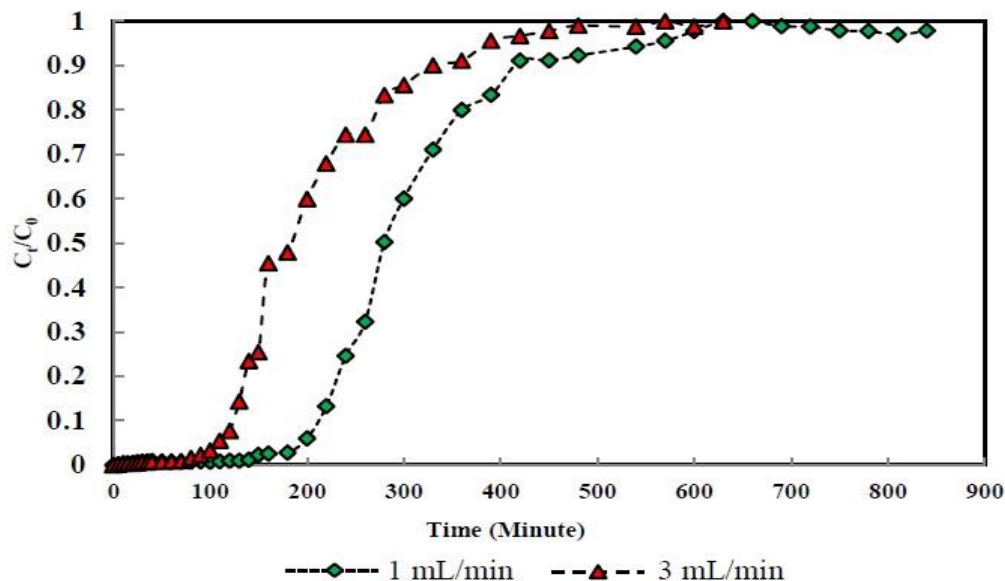


Fig. 5. Breakthrough curves for adsorption of copper (II) for different flow rates (concentration 100 mg/L, pH 5.5, temperature 30 ± 1 °C)

Table 1. Fixed Bed Adsorption Parameters for Cu(II) Adsorption at Different Conditions

Inlet Concentration (mg/L)	Bed Height (cm)	Solution Flow Rate (mL/min)	Breakthrough Time, t_b (min)	Complete Exhaustion Time, t_e (min)	Empty Bed Contact Time, EBCT (min)	Bed Capacity, at $t_{0.5}$ q_{eq} (mg/g)
50	4.5	1	280	870	71.54	4725.43
70	4.5	1	220	750	71.54	5735.05
100	4.5	1	200	660	71.54	6021.94
100	3.0	1	120	570	47.69	5219.31
100	4.5	3	60	630	23.86	5634.51

At the higher inlet concentration, higher equilibrium uptake was observed for the column sorption system. However, the experimental results obtained for adsorption of Cu(II) cations showed that the highest adsorption capacity was obtained using a solution of 100 mg/L as the inlet concentration with a bed height of 4.5 cm and a 1 mL/min flow rate. It was depicted in previous literature that the reduction of the bed height would cause axial dispersion to affect the overall mass transfer process. This causes a reduction in diffusion of the adsorbate (Taty-Costodes *et al.* 2005) and indicates that the solute did not get enough time to diffuse into the whole of the adsorbent mass by using a lower bed height and higher flow rate of adsorbate solution. It can be concluded that the developed column would exhibit better performance by using a lower flow rate (1 mL/min) of the inlet solution.

From Table 1, it is observed that the relatively longer breakthrough time, t_b (min), and exhaustion time, t_e (min) were required for a lower flow rate of inlet solution. By using the higher flow rate of inlet solution (3 mL/min), the equilibrium sorption capacity of the prepared adsorbent was lower for the same bed height (4.5 cm). This was due to inadequate contact time between the solute and the sorbent in the column and less diffusion of the solute into the pores of the adsorbent.

At the end, the solute had to leave the column before equilibrium was reached. This phenomenon is expected and was previously observed for various fixed bed sorption systems (Taty-Costodes *et al.* 2005; Malkoc *et al.* 2006; Padmesh *et al.* 2006). However at a higher flow rate and lower bed height, a lower empty bed contact time (EBCT) was obtained. It was observed that the lower the EBCT values, the lower the diffusion process resulting in a lower adsorption capacity. A similar trend was followed for the sorption of cadmium onto coir pith (Bharathi *et al.* 2011).

Fixed Bed Modeling

For the successful design of a fixed bed column adsorption process, the concentration-time profile or breakthrough curve should be analyzed carefully. Three different kinetic models were implemented to explain the column dynamic process here. Based on drinking water quality standards, the sorption performance of the cations through the column was analyzed by Thomas, Yoon Nelson, and Bohart-Adams models at concentration ratio parameters of $C_t/C_0 > 0.05$ until 10% breakthrough when the ratio was $C_t/C_0 > 0.90$ (Naja and Volesky 2006; Mohan and Sreelakshmi 2008). Model parameters were calculated by using Sigma Plot, Version 10.

Breakthrough curve analysis using Thomas Model

The Thomas model can explain the plug flow behavior of the fixed bed. It is based on the Langmuir isotherm for equilibrium systems and follows second-order reversible reaction kinetics. It describes the adsorption-desorption process where no axial dispersion is present. The linearized form of the Thomas model can be expressed as follows (Eq. 4):

$$\ln \left[\left(\frac{C_0}{C_t} \right) - 1 \right] = \left(\frac{k_{Th} q_0 m}{Q} \right) - \left(\frac{k_{Th} q_0 V_{eff}}{Q} \right) \quad (4)$$

Here, k_{Th} , (mL/mg-min) is the Thomas rate constant and q_0 (mg/g) is the equilibrium uptake of Cu(II) cations. The amount of activated adsorbent packed inside the column is denoted by m (mg/g). C_0 (mg/L) is the influent cation concentration; C_t (mg/L) is the outlet concentration at time t , and, Q (mL/min) is the flow rate.

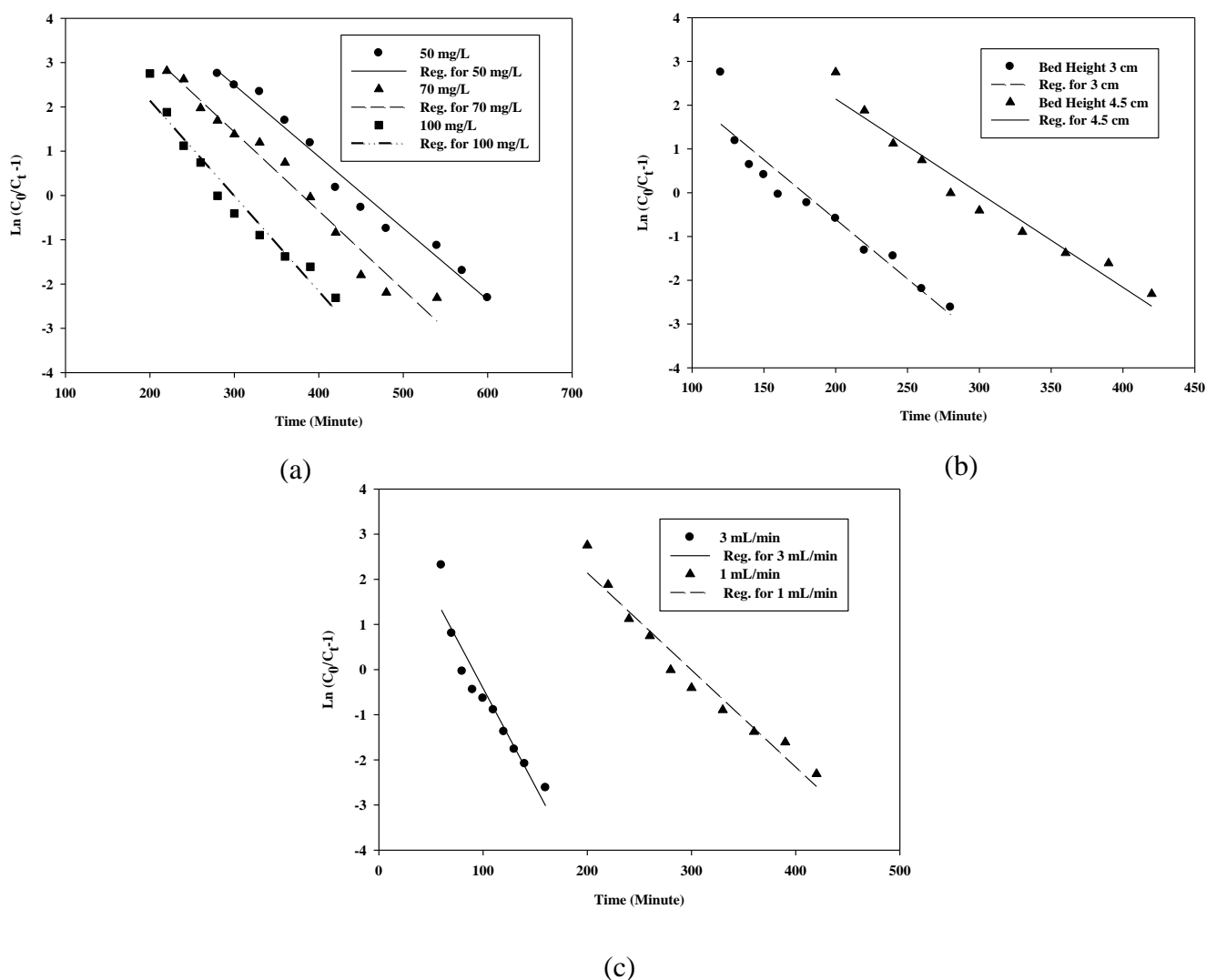


Fig. 6. Linear regression analysis for breakthrough curve modeling by the Thomas model at (a) different concentrations (b) different bed heights (c) different flow rates

The experimental data were fitted with the linear form of the Thomas model. The model constants, k_{th} and q_0 , were calculated from slope and intercepts of the linear plots of $\ln[(C_0/C_t)-1]$ against time, t , using values from the column experiments (Fig. 6). Calculated parameters from the linear regression analysis are summarized in Table 2.

Table 2. Thomas Model Parameters for Copper (II) at Different Conditions Using Linear Regression Analysis

Initial Concentration (mg/L)	Bed Height (cm)	Flow Rate (ml/min)	k_{th} (mL/min-mg) $\times 10^{-4}$	q_0 (mg/g)	R^2
50	4.5	1	3.20	4725.43	0.980
70	4.5	1	2.43	5735.05	0.970
100	4.5	1	2.40	6021.94	0.926
100	3.0	1	2.70	5219.31	0.914
100	4.5	3	4.30	5634.51	0.911

From Table 2, it is apparent that the values of sorption capacity, q_0 (mg/g) increased with an increase in initial concentration of Cu(II) cations from 50 mg/L to 100 mg/L for a fixed bed height of 4.5 cm and flow rate of 1 mL/min. At the same time for the same concentration (100 mg/L) and bed height (4.5 cm), the values of q_0 (mg/g) decreased with the increase in inlet flow rate from 1 to 3 mL/min. On the contrary, q_0 (mg/g) values increased with increase in bed height. Overall the regression coefficient, R^2 , determined by the Thomas model demonstrated the absence of axial dispersion where the rate limiting step was not predominated by external and internal diffusion (Ahmad and Hameed 2010). A similar trend had also been observed by Baral *et al.* (2009) for sorption studies of Cr(VI) onto *Salvinia cucullata*.

Breakthrough Curve Analysis using the Yoon Nelson Model

Yoon and Nelson developed a relatively simple model to analyze the breakthrough performance of the column (Yoon and Nelson 1984). The model presumes that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent (Baral *et al.* 2009). The linearized model for a single component system is expressed by Eq. 5:

$$\ln \left[\frac{C_t}{C_0 - C_t} \right] = k_{YN}t - \tau k_{YN} \quad (5)$$

Here, k_{YN} (min^{-1}) is the rate constant and τ is the time required for 50% adsorbate breakthrough (Baral *et al.*, 2009). The experimental data were fitted with the Yoon Nelson model to investigate the breakthrough characteristics of Cu(II) ions onto the prepared adsorbent. The values of k_{YN} and τ were calculated from the linear plots of $\ln(C_t/C_0 - C_t)$ versus t (min) at different flow rates, bed heights and initial cation concentrations (Fig. 7). The values of k_{YN} and τ for 50% breakthrough time, $t_{0.5}$ (min) are listed in Table 3.

Table 3. Yoon Nelson Model Parameters for Copper (II) at Different Conditions using Linear Regression Analysis

Initial Concentration (mg/L)	Bed Height (cm)	Flow Rate (mL/min)	k_{YN} (L/min)	τ (min)	R^2
50	4.5	1	0.016	459.18	0.980
70	4.5	1	0.017	398.17	0.970
100	4.5	1	0.024	292.66	0.926
100	3.0	1	0.023	268.83	0.970
100	4.5	3	0.043	91.233	0.864

The rate constant, k_{YN} increased with an increase in initial concentration, flow rate, and bed height for column dynamics of Cu(II) cations (Ahmad and Hameed 2010). In this study, the time required for 50% exhaustion of column, decreased with an increase in initial concentration and flow rate. It also decreased with a decrease in bed height.

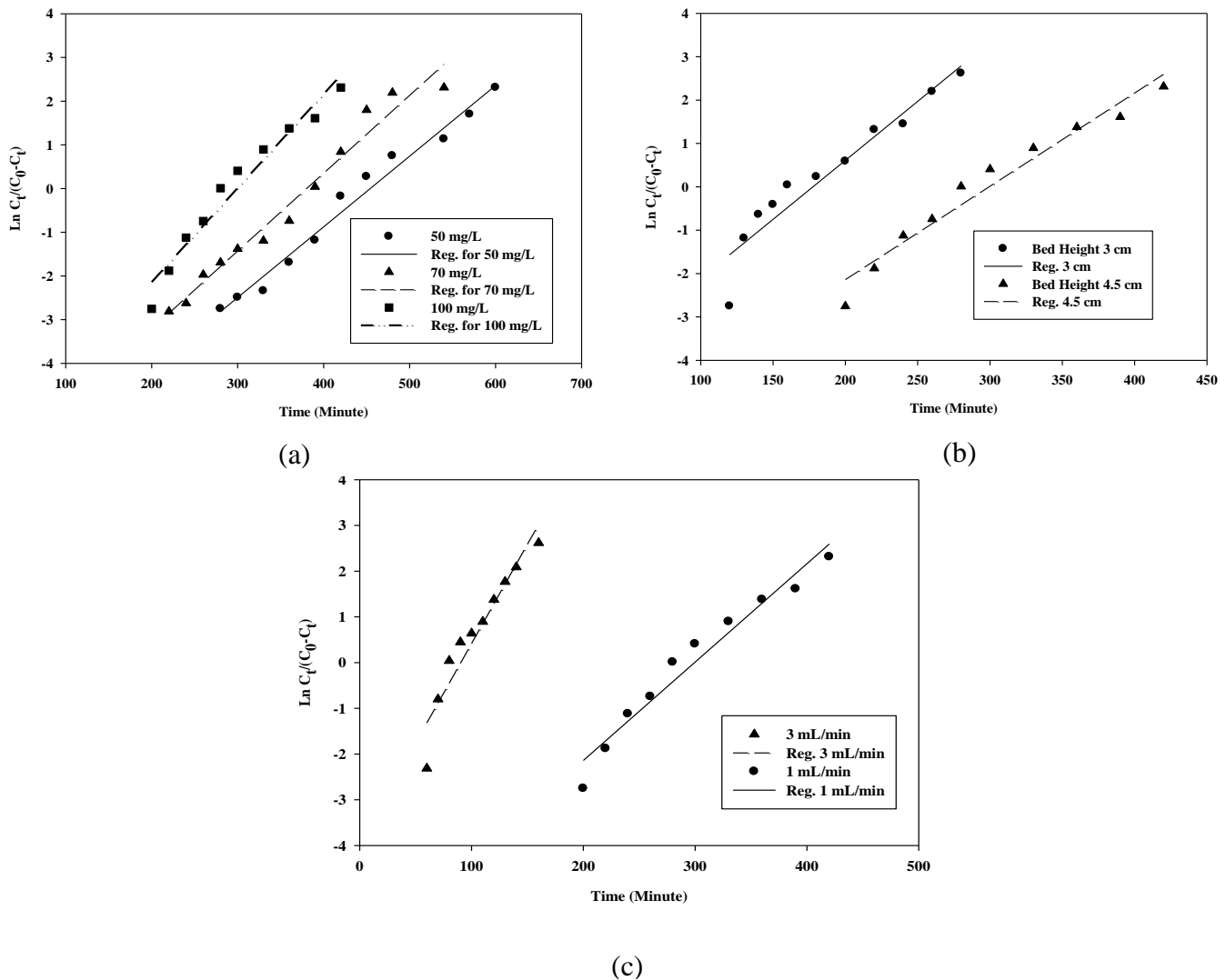


Fig. 7. Linear regression analysis for breakthrough curve modeling by Yoon Nelson model at (a) different concentrations (b) different bed heights (c) different flow rates

Breakthrough Curve Analysis using Adams-Bohart Model

Bohart and Adams proposed a basic equation relating the relationship between C_t/C_o and t (min) in the case of column dynamics studies for the sorption of chlorine on charcoal (Bohart and Adams 1980). This model was developed based on the surface reaction theory. It predicts that equilibrium is not instantaneous; therefore, the rate of adsorption is proportional to both the remaining capacity of the adsorbent and the concentration of the adsorbate (Goel *et al.* 2005). The mathematical equation of the model can be written as (Eq. 6) (Aksu and Gonen 2004):

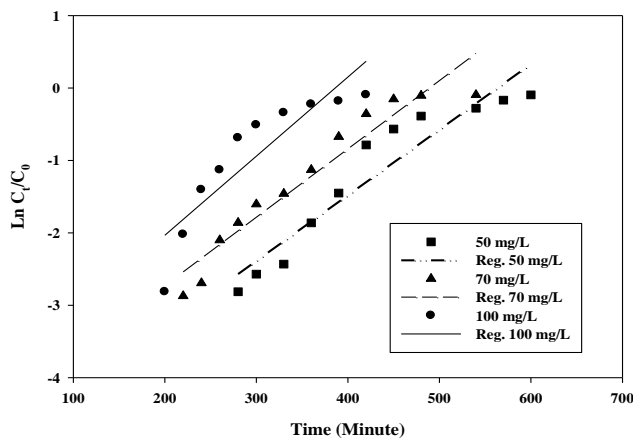
$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB}C_o t - k_{AB}N_o\left(\frac{z}{U_o}\right) \tag{6}$$

Here, C_o and C_t are the inlet and outlet adsorbate concentrations, z (cm) is the bed height, and U_o (cm/min) is the superficial velocity. N_o (mg/L) is the saturation concentration, and k_{AB} (L/mg min) is the mass transfer coefficient (Baral *et al.* 2009).

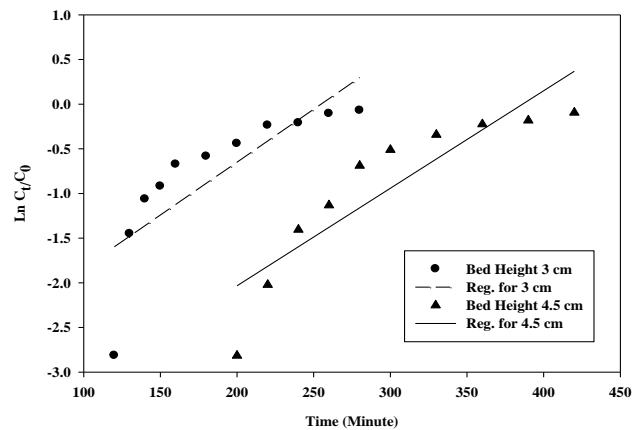
Table 4. Adams-Bohart Parameters for Copper (II) at Different Conditions Using Linear Regression Analysis

Initial Concentration (mg/L)	Bed Height (cm)	Flow Rate (mL/min)	k_{AB} (L/mg-min) x 10^{-4}	N_o (mg/L)	R^2
50	4.5	1	1.80	396.503	0.902
70	4.5	1	1.29	501.725	0.925
100	4.5	1	1.20	559.461	0.737
100	3.0	1	1.10	575.240	0.656
100	4.5	3	1.70	616.339	0.644

The Adams-Bohart model is a comprehensive model for evaluating continuous flow sorption systems in a column. However, its legitimacy is limited to within a certain range. The values of R^2 reveal the lack of applicability of the model (Fig. 8).



(a)



(b)

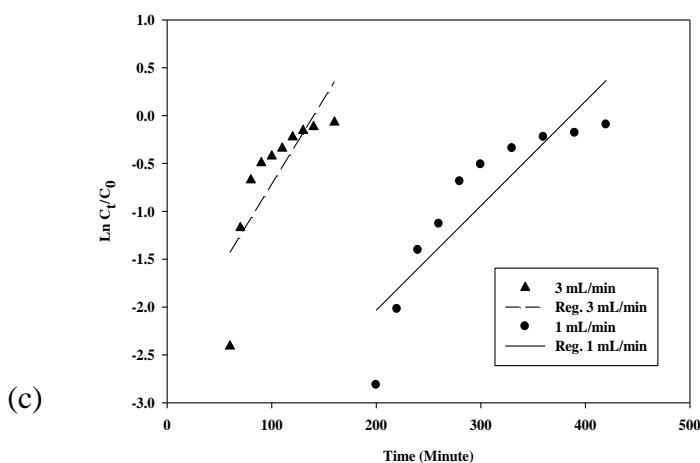


Fig. 8. Linear regression analysis for breakthrough curve modeling by Adams-Bohart model at (a) different concentrations (b) different bed heights (c) different flow rates

It was observed that the mass transfer coefficient increased with an increase in bed height and flow rate but decreased with an increase in initial concentration (Table 4). This implied that the reaction kinetics was strongly influenced by external mass transfer (Ahmad and Hameed 2010). However, the sorption capacity, N_0 , increased with increasing initial concentration and flow rate but reduced slightly for increasing bed height. A similar trend was observed for sorption of Cr(VI) onto thermally activated weed where, by increasing the bed height from 2 to 4 cm, N_0 decreased significantly (Baral *et al.* 2009).

Column Regeneration Studies

Elution of metallic cations is very important for the reusability of exhausted adsorbent as well as commercial viability of the process. To test the reusability of the prepared adsorbent, it was subjected to successive adsorption–desorption cycles using 1 M HNO_3 acid as the eluting agent. The eluting agent was passed inside the column at a flow rate of 3 mL/min for 16 h. The elution process was carried out three times and the percentage adsorption/desorption values were calculated in relation to the original amount of adsorbent. The regeneration efficiencies were calculated using Eq. 2 and summarized in Table 5.

Table 5. Regeneration and Reusability of the Activated Adsorbent

Metal	Cycle No	Breakthrough Time (min)	Breakthrough Uptake (mg/g)	Bed Exhaustion time (min)	Regeneration Efficiency (%)
Copper (II)	1	200	6021.94	660	original
	2	160	4543.40	480	75.44
	3	120	3876.71	260	64.38
	4	90	2098.82	160	34.85

Referring to Table 5, it was observed that exhaustion time and column capacity at 50% breakthrough decreased after each cycle. This is attributed to the undesirable effect of the acid eluting agent on the surface functional groups or binding sites. The column capacity has been found to decrease drastically after the fourth cycle. This reflects that the

properties of the prepared activated adsorbent was deteriorated by acid treatment. A similar trend of desorption was observed for regeneration of lead (II) by using a coconut shell based granular activated carbon (Goel *et al.* 2005).

CONCLUSIONS

The research findings presented herein showed that the lignocellulosic wastes of mangostene exocarp can be converted to granular activated carbon and used successfully to remove Cu(II) cations from wastewater by using a fixed bed column.

1. The removal efficiency of Cu(II) cations was found to increase with an increase in sorbent amount (bed height) but decreased with an increase in both inlet concentration and flow rate of the adsorbate.
2. The experimental data obtained here were fitted with Adams-Bohart, Thomas, and Yoon-Nelson models. Significant features of the different models such as rate constant (Adams-Bohart model), adsorption capacity (Thomas model), and time for 50% breakthrough (Yoon Nelson model) were determined by linear regression analysis. The Yoon Nelson and Thomas models best described the experimental data.
3. Breakthrough time was found to decrease with increase in initial metal ion concentration and flow rate but increased with an increase in bed height.
4. Desorption and regeneration of the cation loaded adsorbent was carried out to observe the suitability of the adsorbent. Based on desorption and regeneration studies, it was concluded that the activated carbon obtained here can be used in up to three cycles, after which the adsorption performance declined significantly.

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REFERENCES CITED

- Adinata, D., Daud, M. A. W., and Aroua, M. K. (2007). "Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3 ," *Bioresour. Technol.* 98, 145-149. DOI: 10.1016/j.biortech.2005.11.006.
- Ahmad, A. A., Hameed, B. H., and Ahmad, A. L. (2009). "Removal of disperse dye from aqueous solution using waste-derived activated carbon: Optimization study," *J. Hazard. Mater.* 170, 612-619. DOI: 10.1016/j.jhazmat.2009.05.021.
- Ahmad, A. A., and Hameed, B. H. (2010). "Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste," *J. Hazard. Mater.* 175, 298-303. DOI: 10.1016/j.jhazmat.2009.10.003.

- Aksu, Z., and Gonen, F. (2004). "Biosorption of phenol by immobilized activated sludge in a continuous packed bed prediction of breakthrough curves," *Process Biochemistry* 39, 599-613. DOI: 10.1016/S0032-9592(03)00132-8.
- Arami-Niya, A., Faisal, A., Mohammad, S. S., Wan Daud, W. M. A., and Sahu, J. N. (2012). "Optimization of synthesis and characterization of palm shell based bio-chars as a by-product of bio-oil production process," *BioResources* 7(1), 246-264.
- Azargohar, R., and Dalai, A. K. (2005). "Production of activated carbon from Luscar char: experimental and modelling studies," *Micropor. Mesopor. Mater.* 85, 219-225. DOI: 10.1016/j.micromeso.2005.06.018.
- Baral, S. S., Das, N., Ramulu, T. S., Sahoo, S. K., Das, S. N., and Chaudhury, G. R. (2009). "Removal of Cr(VI) by thermally activated weed *Salvinia cucullata* in a fixed-bed column," *J. Hazard. Mater.* 161, 1427-1435. DOI: 10.1016/j.jhazmat.2008.04.127.
- Bharathi, K. S., Badabhagni, N., Nidheesh, P. V., Gandhimathi, R., and Ramesh, S. T. (2011). "Breakthrough data analysis of adsorption of Cd(II) on coir pith column," *EJEAFChe.* 10(8), 2638-2658.
- Bohart, G. C. and Adams, E. Q. (1920). "Some aspect of the behavior of charcoal with respect to chlorine," *J. Am. Chem. Soc.* 42, 523-529.
- Chao, C., Yu, C., Zhou, J., Xiang, Y., and Luo, Z. (2014). "Optimization of the three-stage biomass gasification characteristics in high-temperature entrained-flow bed," *BioResources* 9(2), 2621-2633.
- Chen, J. P., and Wang, L. (2004). "Characterization of metal adsorption kinetic properties in batch and fixed-bed reactors," *Chemosphere* 54, 397-404. DOI: 10.1016/S0045-6535(03)00714-8.
- Chen, J. P., and Wang, X. (2000). "Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed-bed columns," *Sep. Purif. Technol.* 19, 157-167 DOI: 10.1016/S1383-5866(99)00069-6.
- Chowdhury, Z. Z., Hamid, S. Bee, Zain, S. M., and Khalid, K. (2014). "Catalytic role of ionic liquids for dissolution and degradation of biomacromolecules," *BioResources* 9(1), 1787-1823
- Chowdhury, Z. Z., Hamid, S. B., Das, R., Hasan, M. R., Zain, S. M., Khalid, K., and Uddin, M. N. (2013). "Preparation of carbonaceous adsorbents from lignocellulosic biomass and their use in removal of contaminants from aqueous solution," *BioResources* 8(4), 6523-6555.
- Chowdhury, Z. Z. "Preparation, characterization and adsorption studies of heavy metals onto activated adsorbent materials derived from agricultural residues," PhD Thesis, University Malaya, Kuala Lumpur, Malaysia, 2013.
- Chowdhury, Z. Z., Zain, S. M., Khan, R. A., and Khalid, K. (2012a). "Process variables optimization for preparation and characterization of novel adsorbent from lignocellulosic waste," *BioResources*, 7(3), 3732-3754.
- Chowdhury, Z. Z., Zain, S. M., Khan, R. A., and Khalid, K. (2012b). "Batch and fixed bed adsorption studies of lead (II) cations from aqueous solutions onto granular activated carbon derived from *Mangostana garcinia* shell," *BioResources* 7(3), 2895-2915.
- Chowdhury, Z. Z., Zain, S. M., Khan, R. A., and Islam, M. S. (2012c). "Preparation and characterizations of fibrous activated carbon from Kenaf for equilibrium adsorption studies of copper from waste water," *Korean J. Chem. Eng.* 29(9), 1187-1195. *KiChE*, DOI:10.1007/s11814-011-02979.

- Chowdhury, Z. Z., Zain, S. M., and Rashid, A. K. (2011a). "Equilibrium isotherm modeling, kinetics, and thermodynamics study for removal of lead from waste water," *E. J. Chem.* 8(1), 333- 339. <http://dx.doi.org/10.1155/2011/184040>.
- Chowdhury, Z. Z., Zain, S. M., Rashid, A. K., and Ahmed, A. A. (2011b). "Equilibrium kinetics and isotherm studies of Cu (II) adsorption from waste water onto alkali activated oil palm ash," *Am. J. Applied Sci.* 8(3), 230-237. DOI: 10.3844/ajassp.2011.230.237.
- Goel, J., Kadirvelu, K., Rajagopal, C., and Carg, V. K. (2005). "Removal of Pb(II) by adsorption using treated granular activated carbon: batch and column studies," *J. Hazard. Mater.* B 125, 211-210. DOI: 10.1016/j.jhazmat.2005.05.032.
- Karacan, F., Ozden, U., and Karacan, S. (2007). "Optimization of manufacturing conditions for activated carbon from turkish lignite by chemical activation using response methodology," *Appl. Therm. Eng.* 27, 1212-1218. DOI:10.1016/j.applthermaleng.2006.02.046.
- Khalili, N. R., Campbell, M., Sandy, G., and Golas, J. (2000). "Production of micro and meso-porous activated carbon from paper mill sludge I. Effect of zinc chloride activation," *Carbon*, 38, 1905-1915. DOI: 10.1016/S0008-6223(00)00043-9.
- Kiran, B. and Kaushik, A. (2008). "Cyanobacterial biosorption of Cr (VI): Application of two parameter and Bohart Adams models for batch and column studies," *Chem. Eng. J.* 144, 391-399. DOI: 10.1016/j.cej.2008.02.003.
- Klassen, C. D. (ed.). (1995). *Casarett & Doull's Toxicology, The Basic Science of Poisons*, Fifth Edition, McGraw-Hill, New York. pp 715.
- Mohan, S., and Sreelakshmi, G. (2008). "Fixed bed column study for heavy metal removal using phosphate treated rice husk," *J. Hazard. Mater.* 153, 75-82. DOI: 10.1016/j.jhazmat.2007.08.021.
- Mondal, M. K. (2009). "Removal of Pb(II) ions from aqueous solution using activated tea waste: Adsorption on a fixed-bed column," *J. Environ. Manage.* 90, 3266-3271. DOI: 10.1016/j.jenvman.2009.05.025.
- Malkoc, E., and Nuhoglu, Y. (2006). "Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed-bed column," *J. Hazard. Mater.* B135, 328-336. DOI: 10.1016/j.jhazmat.2005.11.070.
- Malkoc, E., Nuhoglu, Y., and Abali, Y. (2006). "Cr(VI) adsorption by waste acorn *Quercus ithaburensis* in fixed beds: Prediction of breakthrough curves," *Chem. Eng. J.* 119, 61-68. DOI: 10.1016/j.cej.2006.01.019.
- Naja, G., and Volesky, B. (2006). "Behavior of the mass transfer zone in a biosorption column," *Environ. Sci. Technol.* 40, 3996-4003. DOI: 10.1021/es051542p.
- Padmesh, T. V. N., Vijayaraghavan, K., Sekaran, G., and Velan, M. (2006). "Biosorption of Acid Blue 15 using fresh water macroalga *Azolla filiculoides*: Batch and column studies," *Dyes Pigments* 71, 77-82. DOI: 10.1016/j.dyepig.2005.06.003.
- Salman, J. M., and Hameed, B. H. (2010). "Effect of preparation conditions of oil palm fronds activated carbon on adsorption of bentazon from aqueous solutions," *J. Hazard. Mater.* 175, 133-137. DOI: 10.1016/j.jhazmat.2009.09.139.
- Srinivasakannan, C., and Bakar, M. Z. A. (2004). "Production of activated carbon from rubber wood sawdust," *Biomass Bioenergy* 27, 89-96. DOI: 10.1016/j.biombioe.2003.11.002.
- Stavropoulos, G. G., and Zabaniotou, A. A. (2005). "Production and characterization of activated carbons from olive-seed waste residue," *Micropor. Mesopor. Mater.* 83, 79-85. DOI: 10.1016/j.micromeso.2005.03.009.

- Sudaryanto, Y., Hartono, S. B., Irawaty, W., Hindarso, H., and Ismadji, S. (2006). "High surface area activated carbon prepared from cassava peel by chemical activation," *Bioresour. Technol.* 97, 734-739. DOI: 10.1016/j.biortech.2005.04.029.
- Sumathi, S., Bhatia, S., Lee, K. T., and Mohamed, A. R. (2009). "Optimization of microporous palm shell activated carbon production for flue gas desulfurization: Experimental and statistical studies," *Bioresour. Technol.* 100, 1614-1621. DOI: 10.1016/j.biortech.2008.09.020.
- Tan, I. A. W., Ahmed, A. L., and Hameed, B. H. (2008). "Adsorption of basic dye using activated carbon prepared from oil palm shell: Batch and fixed bed studies," *Desalination* 225, 13-28. DOI: 10.1016/j.desal.2007.07.005.
- Taty-Costodes, V. C., Fauduet, H., Porte, C., and Ho, Y. S. (2005). "Removal of lead (II) ions from synthetic and real effluents using immobilized *Pinus sylvestris* sawdust adsorption on a fixed-bed column," *J. Hazard. Mater.* 123, 135-144. DOI: 10.1016/j.jhazmat.2005.03.032.
- Tay, J. H., Chen, X. G., Jeyaseelan, S., and Graham, N. (2001). "Optimising the preparation of activated carbon from digested sewage sludge and coconut husk," *Chemosphere* 44, 45-51. DOI: 10.1016/S0045-6535(00)00383-0.
- Thomas, H. C. (1944). "Heterogeneous Ion exchange in a flowing system," *J. Am. Chem. Soc.* 66, 1466-1664.
- Tofan, L., Paduraru, C., Irina, V., and Toma, O. (2011). "Waste of rapeseed from biodiesel production as a potential biosorbent for heavy metal ions," *BioResources* 6(4), 3727-3741.
- Treybal, R. E. (1980). *Mass Transfer Operations*, 3rd Ed., McGraw Hill Publisher, New York, USA, pp. 447-522.
- Vinodhini, V., and Das, N. (2010). "Packed bed column studies on Cr(VI) removal from tannery waste water by neem sawdust," *Desalination* 264, 9-14. DOI: 10.1016/j.desal.2010.06.073.
- Wu, Y., Zhang, C., Liu, Y., Fu, Z., Dai, B., and Yin, D. (2012). "Biomass char sulfonic acids (Bc-SO₃H)-catalyzed hydrolysis of bamboo under microwave irradiation," *BioResources* 7(4), 5950-5959.
- Yoon, Y. N. and Nelson, J. H. (1984). "Application of gas adsorption kinetics. Part I. A theoretical model of respirator cartridge service time," *J. Am. Ind. Hyg. Assoc.* 45, 509-516.

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