

## Fixed bed Column Adsorption of Cu (II) onto Maize Tassel-PVA Beads

Mahlatshe M. Sekhula<sup>1</sup>, Jonathan O. Okonkwo<sup>1\*</sup>, Caliphs M. Zvinowanda<sup>1</sup>, Nana N. Agyei<sup>2</sup> and Abdul J. Chaudhary<sup>3</sup>

<sup>1</sup>Department of Environmental, Water & Earth Sciences, Faculty of Science, Tshwane University of Technology, 175 Nelson Mandela Drive, Arcadia Campus, Pretoria, South Africa

<sup>2</sup>Department of Chemistry, University of Limpopo, MEDUNSA Campus, Pretoria, South Africa

<sup>3</sup>Institute for the Environment, Brunel University, Kingston Lane, Uxbridge, Middlesex, UB8 3PH, UK

### Abstract

The intention of this study was to explore the efficacy and feasibility for Cu (II) adsorption onto fixed bed column of maize tassel-PVA beads. The effects of flow rate and bed height were explored. The Thomas, Adams and Bohart and Yoon-Nelson models were analysed to evaluate the column adsorption performance. The adsorption rate constant and correlation coefficient associated to each model for column adsorption was calculated. Thomas model indicated that increase in column height and flow rate increased the values of  $k_{Th}$  and  $q_0$ . Thereafter, the value of  $q_0$  decreased with decreasing bed height. With Adam-Bohart model, the values of  $k_{AB}$  increased as the flow rate and the bed height increased and continued to increase with decrease in bed height. However, the value of  $N_0$  first increased with increase in flow rate and bed height, but later decreased with decrease in bed height. This suggests that the overall system kinetics may have been influenced by external mass transfer, particularly in the initial part of adsorption in the column. In the case of Yoon-Nelson model, the rate constant  $k_{YN}$  and  $\tau$  increased with increase in bed height and flow rate. However, decrease in bed height at a flow rate of  $2.33 \times 10^{-3} \text{ L min}^{-1}$  resulted in an increase in  $\tau$  while the values of  $k_{YN}$  decreased. The three models gave high values of  $R^2$  (0.9694-0.98920), although the Adam-Bohart model values were, on average, the least. Therefore, it can be said that both the Thomas and Yoon-Nelson models describe the behavior of the adsorption of Cu (II) in a fixed-bed column better than Adam-Bohart.

**Keywords:** Maize tassel; Polyvinyl alcohol; Beads; Cu(II) removal; Column studies

### Introduction

Effective removal of trace metal ions from aqueous solution is important in order to protect the environment and to improve the quality of public health. Trace metals such as mercury, lead and cadmium are not biodegradable and are known to bio-accumulate in the food chain. Therefore, the removal of trace metals from the environment, particularly from water, is very important since water is one of the most valuable natural resources. Copper is an essential element in mammalian nutrition as a component of metallo enzymes in which it acts as an electron donor or acceptor. However, exposure to high levels of copper can result in a number of adverse health effects [1]. Hence, the study of removal of copper ions in aqueous system is essential.

Physical and chemical methods have been employed in the removal of trace metals from contaminated water through processes such as chemical precipitation, membrane filtration, ion exchange, and adsorption. One of the new developments in recent years to remove toxic trace metals from aqueous solutions is the use of adsorbents of biological origin, including alginate, dead and living biomass, chitosan, lignin, and others [2]. Agricultural waste products such as maize tassel, rice husks, corn cobs, olive mill products and polymerized orange skin have been reported for their removal of toxic metals from aqueous solutions [3-9].

Maize tassel, a waste biomaterial, is the 'male' flower of the maize plant that forms at the top of the stem. The tassel grows at the apex of the maize stalk and end up as agricultural waste product after being involved in fertilisation. It is discarded by farmers in large quantities with the rest of the plant once the cobs have been harvested. In our earlier studies, we reported the potential of maize tassel to remove trace metals from aqueous solution, physicochemical characterisation of the tassel for texture, microstructure, elemental composition and

thermal stability [8]. However, earlier attempt to use ground maize tassel in column experiments showed that the material was soft and, therefore, clogged columns thus preventing free flow of water. In order to apply this waste material effectively in column experiments, it became necessary to immobilize onto an inert substance which can provide support without the maize tassel losing its capacity to remove metals from aqueous solution. Immobilisation of such material will create material with mechanical strength and rigidity. For this purpose, materials such as Polyvinyl Alcohol (PVA), has been used [10,11]. To date, the immobilisation of maize tassel-PVA for the removal of heavy metals from aqueous solution has not been reported.

Batch experiments are usually conducted to evaluate the ability of a material to adsorb as well as the adsorption capacity of the material. The data obtained from batch experiments are, in most cases, limited to laboratory scale and thus do not provide data which can be accurately applied in industrial systems. Column experiments, on the other hand, are necessary to provide data which can be applied for industrial purposes [12].

In this study, the efficacy and feasibility for Cu (II) adsorption onto fixed bed column of maize tassel immobilised in polyvinyl alcohol matrix to form beads was explored. The effects of flow rate and bed

**\*Corresponding author:** Jonathan O. Okonkwo, Department of Environmental, Water & Earth Sciences, Faculty of Science, Tshwane University of Technology, 175 Nelson Mandela Drive, Arcadia Campus, Pretoria, South Africa, Tel: +27123826245; Fax: +27123826354; E-mail: [OkonkwoOJ@tut.ac.za](mailto:OkonkwoOJ@tut.ac.za)

Received March 19, 2012; Accepted April 21, 2012; Published April 23, 2012

**Citation:** Sekhula MM, Okonkwo JO, Zvinowanda CM, Agyei NN, Chaudhary AJ (2012) Fixed bed Column Adsorption of Cu (II) onto Maize Tassel-PVA Beads. J Chem Eng Process Technol 3:131. doi:10.4172/2157-7048.1000131

**Copyright:** © 2012 Sekhula MM, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

height were investigated. The Thomas, Adam-Bohart and Yoon-Nelson models were employed to evaluate the column adsorption performance. Also scanning electron microscopy was carried out on maize tassel-PVA beads for morphology identification.

## Methods

### Materials and equipment

All chemicals used were of analytical grade and were used without further purification. Polyvinyl alcohol (PVA, 99% hydrolyzed, average molecular weight 89,000-98,000) was obtained from Aldrich Chemical. For column experiments, aqueous samples were pumped through the column with a Watson Marlow 101U/R peristaltic pump (Watson-Marlow limited, England). Microstructure was determined using a JSM-5800LV (JEOL, Japan) scanning electron microscope and a JSM-7500F (JEOL, Japan). Vernier calliper was used to measure the diameter of the maize tassel-PVA beads.

### Preparation of maize tassel powder

Maize tassel collected from the Tshwane University of Technology research farm in Pretoria, South Africa, was first air dried for two days in a fume cupboard and then thoroughly rinsed with copious amounts of deionised water. The material was then placed in an air powered drying hood to remove water. Finally, the tassel was dried in an oven at 105°C for 24 h to expel any residual moisture. The dried material was then milled by a hammer mill model Laboratory Mill 3 100 (Stockholm, Sweden). Thereafter, the milled tassel was sieved to a particle size of 150-500 µm.

### Preparation of maize tassel-PVA beads

The method of preparation was as described by Jin and Bai [10]. Briefly, about 8.50 g of PVA powder was weighed into a 0.25 L beaker containing 0.10 L deionised water. The mixture was stirred at a speed of 800 rpm at 80°C for 5 h and 10 g of sieved tassel powder added to the mixture with stirring. The mixture was stirred for another 1 h until the tassel powder blended well with the PVA and the temperature of the mixture reduced to 50°C. The gel formed was, thereafter, cooled and extruded into small beads. The beads were placed into a beaker containing 99% methanol for 1 h, and later rinsed with deionised water, air dried in a fume cupboard and stored in airtight container before use. The diameters of the beads (5.50 ± 0.48 mm) were measured using a vernier calliper. The PVA beads were prepared in the same but without the addition of maize tassel powder.

### Microstructure analysis

About 1.0 g of maize tassel-PVA beads and 1.0 g of tassel powder were separately mounted onto double sided tape and placed on a special SEM stage. The samples were sputter coated with carbon to avoid sputtering. The surface morphology of the samples was obtained with SEM mode and later changed to EDX mode to obtain the elemental composition of the samples.

### Batch experiment

Batch experiment was first conducted with polyvinyl alcohol beads (PVA), maize tassel powder (MT) and maize tassel-polyvinyl beads (MT-PVA) in order to determine the potential of PVA to adsorb Cu (II) from aqueous solution. About 5.0 g of the aforementioned adsorbents were weighed and added into separate 250 mL solutions containing 20 mg L<sup>-1</sup> of Cu (II) and the pH of the mixture adjusted to 4 with 0.1 M HCl. The mixtures were shaken in an orbital shaker

at a speed of 200 rpm under room temperature for 1-2 h. Samples were taken at predetermined time intervals for the analysis of Cu (II) ion concentrations in the solution until adsorption equilibrium was reached. Cu (II) concentrations were analyzed by using a Varian 220 FS Flame Atomic Absorption Spectrometer (FAAS) coupled to an SPS5 (sample preparation system) and a Sample Introduction Pump System (SIPS). The adsorbed amount of Cu (II) per unit weight of beads and powder were calculated from equation 1.

$$Q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where  $Q_e$  is the metal adsorbed in mg g<sup>-1</sup>;  $C_i$  and  $C_e$  are the initial and equilibrium concentrations of metal (mg L<sup>-1</sup>);  $V$  is the volume of the solution (L), and  $m$  is the mass of the biosorbent (g).

### Column experiments

A glass column of internal diameters (I.D) of 25 mm and 20 cm in length, 20 mg L<sup>-1</sup> of Cu (II) solutions at flow rates of 0.80 mL min<sup>-1</sup> and 2.33 mL min<sup>-1</sup> and column bed heights of 5 cm and 10 cm were used for the experiment. The columns were packed by placing weighed layers of glass wool before and after packing the maize tassel-PVA beads. All experiments were conducted at room temperature and the direction of flow was from bottom to top. The treated metal solution was collected at the outlet at different time intervals and analysed. The column was run at a predetermined pH of 4.0 as established in our previous study [8]. The experimental conditions for the column runs are shown in Table 1.

### Kinetic models

In this study, three models namely Thomas [13], Adam-Bohart [14] and Yoon-Nelson [15] models were used for kinetic studies. The Thomas solution is one of the most widely used models in assessing column performance. The expression by Thomas for an adsorption column is given as follows:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{TH}q_oX}{Q} - \frac{k_{TH}C_o}{Q}V_{eff} \quad (2)$$

where  $C_t$  is the effluent concentration at time  $t$  (mg L<sup>-1</sup>),  $C_o$  the influent concentration (mg L<sup>-1</sup>),  $k_{th}$  is the Thomas rate constant (L min<sup>-1</sup> mg<sup>-1</sup>),  $q_o$  the equilibrium uptake per g of the adsorbent (mg g<sup>-1</sup>),  $x$  the amount of adsorbent in the column (g),  $V_{eff}$  the effluent volume (L) and  $v$  is the flowrate (L min<sup>-1</sup>). The kinetic coefficient  $k_{th}$  and the adsorption capacity of the column  $q_o$  can be determined from a plot of  $C_t/C_o$  against  $t$  at a given flow rate using linear regression.

The Adam-Bohart model is used for the description of the initial part of the breakthrough curve. The data obtained in column in continuous mode studies was used to calculate maximum solid phase concentration of Cu (II) on maize tassel-PVA beads. The Adam-Bohart expression is given as:

Column No	Height (cm)	Column ID (mm)	pH	Flow rate (x 10 <sup>-3</sup> L min <sup>-1</sup> )	Feed Concentration (mg L <sup>-1</sup> )
1	5.0	25	4	0.8	20.0
2	0.0	25	4	2.33	20.0
3	5.0	25	4	2.33	20.0

Table 1: Experimental conditions for column runs.

$$\ln\left(\frac{C_o}{C_t} - 1\right) = k_{AB}N_o \frac{Z}{F} - k_{AB}C_o t \quad (3)$$

where  $C_t$  and  $C_o$  are the effluent and influent concentrations ( $\text{mg L}^{-1}$ ) at time  $t$  and zero,  $k_{AB}$  is the kinetic constant ( $\text{L mg}^{-1} \text{min}^{-1}$ ),  $t$  is time (min),  $N_o$  is the saturation concentration ( $\text{mg L}^{-1}$ ) and  $Z$  is the bed depth of column (cm),  $F$  is the linear flow rate ( $\text{L min}^{-1}$ ). Parameters describing the characteristic operations of the column ( $k_{AB}$  and  $N_o$ ) were determined from a linear plot of  $\ln(C_t/C_o)$  against time ( $t$ ), as the intercept and slope respectively.

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

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \tau k_{YN} - k_{YN} t \quad (4)$$

where  $C_t$  and  $C_o$  are the effluent and influent concentrations ( $\text{mg L}^{-1}$ ) at time  $t$  and zero,  $k_{YN}$  ( $\text{L min}^{-1}$ ) is the Yoon-Nelson constant,  $\tau$  (min) is the time required for 50% adsorbate breakthrough. From a linear plot of  $\ln[C_t/(C_o - C_t)]$  against sampling time ( $t$ ), values of  $k_{YN}$  and  $\tau$  were determined from the intercept and slope of the plot.

## Results and Discussions

### Maize tassel-PVA beads

The beads formed from the immobilization of powdered maize tassel in polyvinyl alcohol matrix were reasonably spherical in shape, and their diameters were in the range of  $5.50 \pm 0.48$  mm.

### Microstructure analysis

Figure 1 shows scanning electron micrographs of powdered tassel (a) and maize tassel-PVA beads (b). From Figure 2, maize tassel powder appeared as elongated fibrous particles which are bound tightly to PVA, although the elongated shape was still maintained. The SEM images verified that the addition of PVA made the maize tassel become much denser, as shown in Figure 1.

### Batch experiment

The results of the batch experiments with polyvinyl alcohol beads, maize tassel powder and maize tassel-polyvinyl alcohol beads are shown in Figure 2. From Figure 2, the amount of Cu (II) ions adsorbed by PVA beads was very insignificant compared to the adsorption exhibited by maize tassel powder and maize tassel-PVA beads. The amounts of Cu (II) adsorbed by maize tassel powder and maize tassel-PVA beads were  $0.50 \text{ mg g}^{-1}$  and  $0.52 \text{ mg g}^{-1}$  respectively. Further experiments were conducted using only maize tassel-PVA beads.

### Effect of influent flow rate on Cu (II) adsorption by maize tassel-PVA beads

The column adsorption study was conducted at different influent flow rates of  $8.0 \times 10^{-4}$  and  $2.33 \times 10^{-3} \text{ L min}^{-1}$  using initial Cu (II) concentration of  $20 \text{ mg L}^{-1}$ , bed height of 5 cm, pH 4 and room temperature of  $25^\circ\text{C}$ . Figure 3 shows the resultant breakthrough curve in which the breakthrough occurred faster at higher flow rate of  $2.33 \times 10^{-3} \text{ L min}^{-1}$  than at lower flow rate of  $8.0 \times 10^{-4} \text{ L min}^{-1}$ . The faster breakthrough curve exhibited by flow rate  $2.33 \times 10^{-3} \text{ L min}^{-1}$ , was

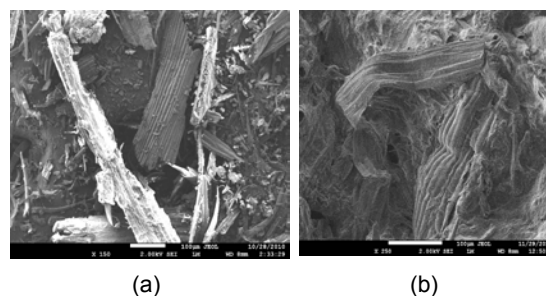


Figure 1: (a) SEM micrographs showing the surface morphologies of maize tassel powder and (b) Maize tassel PVA beads.

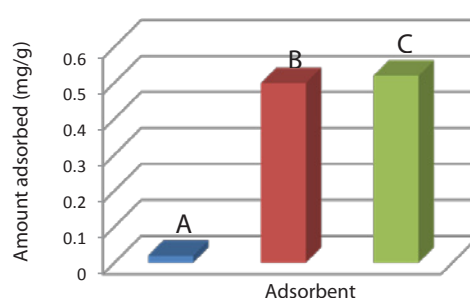


Figure 2: (A) Adsorption of Cu(II) by polyvinyl alcohol only, (B) Maize tassel powder only and (C) Maize tassel-PVA beads.

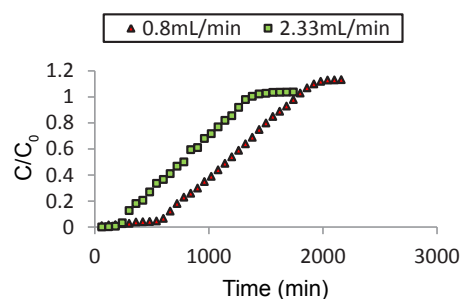


Figure 3: Breakthrough curves for Cu(II) adsorption by maize tassel-PVA beads at different flow rates (Cu(II) concentration  $20 \text{ mg L}^{-1}$ , column height 5 cm, pH 4 and  $25^\circ\text{C}$ ).

attributed to faster movement of the adsorption zone along the bed, thus reducing the contact time between the influent, Cu (II) and the adsorbent, maize tassel-PVA beads. On the other hand, the gradual breakthrough curve for flow rate of  $8.0 \times 10^{-4} \text{ L min}^{-1}$  suggested longer residence time of the influent in the column. Similar trends have been reported by researchers using activated rice husk to remove Cu (II) and dye from aqueous solution [16, 17]. It can also be observed from Figure 3, that the maximum  $C/C_o$  value for flow rate of  $2.33 \times 10^{-3} \text{ L min}^{-1}$  is lower than that of  $8.0 \times 10^{-4} \text{ L min}^{-1}$ . This can be attributed to the reduction of adsorption efficiency since the contact time of the influent in the column was low.

### Effect of bed height on Cu (II) adsorption by maize tassel-PVA beads

The effects of bed heights of 5.0 cm and 10.0 cm were studied at influent concentration of  $20 \text{ mg L}^{-1}$ ,  $2.33 \times 10^{-3} \text{ L min}^{-1}$  flow rate and pH 4. From Figure 4, the breakthrough time increased with bed height.



This was attributed to the fact that as the bed height increased from 5 to 10 cm, Cu (II) had more contact time with the maize tassel beads which resulted in higher removal of Cu (II) ions from the column. Furthermore, the slope of the breakthrough curves decreased with increase in bed height as a result of broadened influent movement zone. Higher Cu (II) removal was observed for bed height of 10.0 cm because of the increase in the bed surface which provided more binding sites for the adsorption of Cu (II) onto maize tassel-PVA beads. It should be noted that the breakthrough curves for bed height 5 cm in Figure 4 and the  $2.33 \times 10^{-3} \text{ L min}^{-1}$  in Figure 3 were performed under identical conditions. However, the dissimilarities observed on the curves may be due to variability of flow rates during experimentation as well as the non-reproducibility in the production of bead used in this study.

### Thomas model

The behaviour of the column was modelled using the Thomas model. The influences of flow rate and bed height on the adsorption of Cu (II) with maize tassel-PVA were studied. The results are shown in Table 2. The Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting step [17]. The column data were fitted 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 equation (2) and the results are shown in Table 2. As can be seen in Table 2, as the column height and flow rate increased the values of  $k_{th}$  and  $q_0$  increased. Thereafter, the value of  $q_0$  decreased with decreasing bed height. The values of  $k_{th}$  obtained in the present study are within the range reported in a fixed bed study for the removal of Cu (II) from aqueous solution using rice

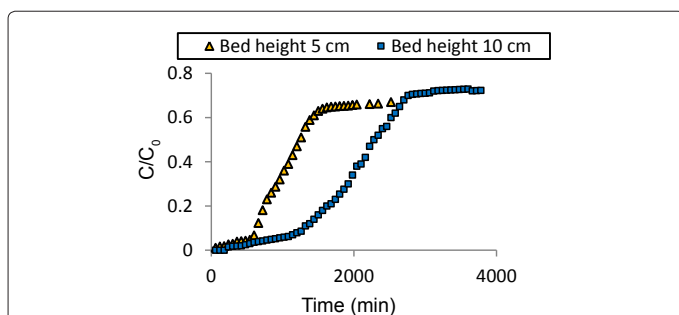


Figure 4: Breakthrough curves for Cu(II) adsorption by maize tassel-PVA beads at different bed heights (Cu(II) concentration  $20 \text{ mg L}^{-1}$ , flow rate  $2.33 \times 10^{-3} \text{ L min}^{-1}$ , pH 4 and  $25^\circ\text{C}$ ).

Inlet Concentration ( $\text{mg g}^{-1}$ )	pH	Bed height (cm)	Flow rate ( $\times 10^{-3} \text{ L min}^{-1}$ )	$k_{th}$ ( $\times 10^{-3} \text{ L min}^{-1} \text{ mg}^{-1}$ )	$Q_0$ ( $\text{mg g}^{-1}$ )	$R^2$
20	4.0	5.0	0.80	0.20304	3.98	0.9806
20	4.0	10.0	2.33	0.20468	7.766	0.9858
20	4.0	5.0	2.33	1.0995	3.102	0.9745

Table 2: Thomas model parameters at different conditions using linear regression analysis.

Inlet Concentration ( $\text{mg g}^{-1}$ )	pH	Bed height (cm)	Flow rate ( $\times 10^{-3} \text{ L min}^{-1}$ )	$k_{AB}$ ( $\times 10^{-4} \text{ L mg}^{-1} \text{ min}$ )	$N_0$ ( $\text{mg L}^{-1}$ )	$R^2$
20	4.0	5.0	0.80	1.85	2670	0.9827
20	4.0	10.0	2.33	2.35	9570	0.9826
20	4.0	5.0	2.33	9.25	116	0.9694

Table 3: Adam-Bohart model parameters at different conditions using linear regression analysis.

Inlet Concentration ( $\text{mg g}^{-1}$ )	pH	Bed height (cm)	Flow rate ( $\times 10^{-3} \text{ L min}^{-1}$ )	$k_{YN}$ ( $\text{L min}^{-1}$ )	$\tau$ ( $\text{mg g}^{-1}$ )	$R^2$
20	4.0	5.0	0.8	0.004	1176	0.9893
20	4.0	10.0	2.33	0.048	1513	0.9806
20	4.0	5.0	2.33	0.0194	3601	0.9727

Table 4: Yoon-Nelson model parameters at different conditions using linear regression analysis.

husk based activated carbon [16], ammonium ion removal by zeolite 13X [18] and adsorption of Acid Yellow 17 Dye onto Tamarind seed powder [19], but significantly lower than the values reported for the removal of methylene blue from aqueous solution using rice husk [20]. However, the  $q_0$  values obtained in the present study are significantly lower than the values reported [17,18,19]. The  $R^2$  values ranged from 0.9745-0.9858, indicating good linearity. It can, therefore, be said that the high  $R^2$  value indicates that the Thomas model equations of linear regression analysis describes the breakthrough data under the studied conditions.

### Adams-Bohart model

This model assumes that the adsorption process is continuous and that equilibrium is not attained instantaneously. The Adam-Bohart adsorption model was applied to experimental data for the breakthrough curve. After applying equation (3) to the experimental data, a linear relationship was found for the time for breakthrough. For all breakthrough curves, respective values of  $N_0$  and  $k_{AB}$  were calculated and presented in Table 3. From Table 3, it can be seen that the values of  $k_{AB}$  increased as the flow rate and the bed height increased and continued to increase with decrease in bed height. However, the value of  $N_0$  first increased with increase in flow rate and bed height, but later decreased with decrease in bed height. This suggests that the overall system kinetics may have been influence by external mass transfer, particularly in the initial part of adsorption in the column [20]. The values of saturation concentration,  $N_0$ , obtained in the present study are significantly higher than the values reported [16]. The correlation coefficient,  $R^2$  values were between 0.9694-0.9827.

### Yoon-Nelson model

The values of  $k_{YN}$  and  $\tau$  are listed in Table 4. From Table 4, the rate constant  $k_{YN}$  and  $\tau$  increased with increase in bed height and flow rate. However, decrease in bed height at a flow rate of  $2.33 \times 10^{-3} \text{ L min}^{-1}$  resulted in an increase in  $\tau$  while the values of  $k_{YN}$  decreased. These observations are in agreement with a fixed bed column adsorption of Acid Yellow 17 Dye onto Tamarind seed powder [16].

### Conclusion

The present study demonstrated the ability of maize tassel-PVA to remove Cu (II) from aqueous solution in a column model. The change in flow rate and column height influenced the amount of Cu (II) adsorbed. The results obtained with maize tassel-PVA were in agreement with studies reported in the literature. The adsorption models applied to evaluate the performance of the column describe the fixed bed column well. However, the value of  $R^2$  for Adam-Bohart model was generally lower than Thomas and Yoon-Nelson models under the same experimental conditions. Therefore, it can be concluded that both the Thomas and Yoon-Nelson models describe the behaviour of the adsorption of Cu (II) in a fixed-bed column better than Adam-Bohart.

## Acknowledgements

This Research was supported by the International Cooperation Unit (facilitated by Dr B. Kgarebe) of the Organisation for the Prohibition of Chemical Weapon (OPCW), Tshwane University of Technology and National Research Foundation of South Africa.

## References

1. Stern BR, Solioz M, Krewski D, Aggett P, Aw TC, et al. (2007) Copper and human health: biochemistry, genetics, and strategies for modeling dose-response relationships. *J Toxicol Environ Health B Crit Rev* 10: 157-222.
2. Bailey SE, Olin TJ, Bricka RM, Adrian DD (1999) A review of potentially low-cost sorbents for heavy metals. *Water Research* 33: 2469-2479.
3. Lokatos J, Brown SD, Snape CE (2002) Coals as sorbents for the removal and reduction of hexavalent chromium from aqueous waste streams. *Fuel* 81: 691-698.
4. Doyurum S, Celik A (2006) Pb (II) and Cd (II) removal from aqueous solutions by olive cake. *J Hazard Mater* 138: 22-28.
5. Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresour Technol* 98: 2243-2257.
6. Mohan D, Pittman CU Jr (2006) Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *J Hazard Mater* 137: 762-811.
7. Šćiban M, Klačnja M, Škrbić B (2008) Adsorption of copper ions from water by modified agricultural by-products. *Desalination* 229: 170-180.
8. Zvinowanda CM, Okonkwo OJ, Agyei NM, Shabalala PN (2009) Physicochemical characterization of maize tassel as an adsorbent. I. Surface texture, microstructure, and thermal stability. *J Appl Polymer Sci* 111: 1923-1930.
9. Zvinowanda CM, Okonkwo JO, Sekhula MM, Agyei NM, Sadiku R (2009) Application of maize tassel for the removal of Pb, Se, Sr, U and V from borehole water contaminated with mine wastewater in the presence of alkaline metals. *J Hazard Mater* 164: 884-891.
10. Jin L, Bai R (2002) Mechanisms of lead adsorption on chitosan /PVA hydrogel beads. *Langmuir* 18: 9765- 9770.
11. Khoo K, Ting Y (2001) Biosorption of Gold by immobilized fungal biomass. *Biochem Eng J* 8: 51-59.
12. Wang S, Li H, Xie S, Liu S, Xu L (2006) Physical and chemical regeneration of zeolitic adsorbents for dye removal in wastewater treatment. *Chemosphere* 65: 82-87.
13. Thomas HC (1944) Heterogeneous ion exchange in a flowing system. *J Am Chem Soc* 66: 1664-1666.
14. Bohart G, Adams EQ (1920) Some aspects of the behaviour of charcoal with respect to chlorine. *J Am Chem Soc* 42: 523-544.
15. Yoon YH, Nelson JH (1984) Application of gas adsorption kinetics--II. A theoretical model for respirator cartridge service life and its practical applications. *Am Ind Hyg Assoc J* 45: 517-524.
16. Patel H, Vashi RT (2012) Fixed bed column adsorption of ACID Yellow 17 dye onto Tamarind Seed Powder. *Can J Chem Eng* 90: 180-185.
17. Yahaya NKEM, Abustana I, Latiffa MFPM, Bello OS, Ahmad MA (2011) Fixed-bed column study for Cu (II) removal from aqueous solutions using rice husk based activated carbon. *International Journal of Engineering & Technology* 11: 248-252.
18. Han R, Wang Y, Yu W, Zou W, Shi J, et al. (2007) Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column. *J Hazard Mater* 141: 713-718.
19. Zheng H, Han L, Ma H, Zheng Y, Zhang H, et al. (2008) Adsorption characteristics of ammonium ion by zeolite 13X. *J Hazard Mater* 158: 577-584.
20. Guibal E, Lorenzelli R, Vincent T, Cloirec PL (1995) Application of silica gel to metal ion sorption: static and dynamic removal of uranyl ions. *Environmental Technology* 16: 101-114.