IOSR Journal Of Pharmacywww.iosrphr.org
(e)-ISSN: 2250-3013, (p)-ISSN: 2319-4219
PP. 69-78

Analysis of packed bed adsorption column with nanochitosan /sodium alginate/ microcrystalline cellulose bead for copper (II) removal from aqueous solution

[1]K. Vijayalakshmi, [2]K.Sangeetha and [2]Dr. P.N. Sudha
[1,2] PG & Research department of chemistry, DKM College for women, Tamilnadu, Vellore-1

Abstract: *In the current research, removal of copper(II) from aqueous solution using nanochitosan/sodium alginate/microcrystalline cellulose bead as an adsorbent is studied in packed bed with respect to various parameters like initial concentration, flow rate and bed height. The breakthrough characteristics of the adsorption were studied by describing the breakthrough curve. The fixed bed column experiments carried out as a function of NCS/SA/MC bed height (1cm and 1.5 cm), flow rate (1.0 ml/min and 1.5 ml/min) and inlet metal ion concentration (200mg/L and 300 mg/L) reveals that the breakthrough time and exhaustion time were increased with increase in bed height and decreased with increasing influent metal ion concentration and flow rates. The prediction of the adsorption performance and the capacity in a fixed-bed column evaluated by three well-established fixed-bed adsorption kinetic models namely Thomas, Yoon Nelson and Adam Bohart models indicate that, when compared to the other models the Thomas and Yoon nelson model fitted well with higher coefficients of correlation $R^2 \geq 0.83$ at different conditions. These findings suggested that the prepared NCS/SA/MC bead has a great potential in removing the copper (II) from aqueous solution in continuous mode using fixed bed column.*
Keywords: *Packed bed column, Breakthrough curve, copper (II), Kinetic model, adsorption*

I. INTRODUCTION

On a global scale, recently the environmental pollution by industries via effluent discharge has become a threat to plants and animals, and may ultimately threaten the quality of human life [1]. Among the various pollutants in industrial effluents, due to its bioaccumulative and toxic nature, the heavy metals were considered to be priority pollutants [2] and hence the purification of these wastewaters prior to their discharge into water bodies becomes necessary.The industrial effluents contain numerous heavy metals such as Cd, Cu, Pb etc. and among the various heavy metals, copper is one of the most ubiquitous contaminants in the soil and aqueous environments with a lot of hazardous effect towards human health. Numerous wastewater treatment methods developed by many researchers including precipitation, chemical oxidation, adsorption, reduction, ion exchange, electrodialysis etc., were extremely expensive or inefficient [3]. Among the various techniques, the wastewater treatment by adsorption is quite very effective and has been cited by environmental protection agency as being one of the best available environmental control technologies due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness[4] and hence adsorption was utilized in this present work.

Recently, there has been an increasing emphasis on the adsorbent with low cost for the heavy metal ions removal. Especially due to their extraordinary affinity to heavy metal ions, the naturally occurring polysaccharides such as alginic acid and chitosan have been recognized as the most effective adsorbents to eliminate low levels of heavy metal ions from waste water stream [5]. In order to improve the features of chitosan as an effective adsorbent with high selectivity and adsorption capacity, chemical modification has been done.The adsorption capacity can be controlled by sorbent particle size and so in this research the nanochitosan (NCS) were produced from chitosan by experimental approach.Alginate, a linear polysaccharide composed of alternating blocks of 1-4 linked α-L-guluronic and β-D-mannuronic acid fragments. Due to their high affinity for chelation with metal cations, the alginate was proved to be excellent materials for water purification . The agricultural by-products (banana, jute sisal, coir etc) are classes of materials evaluated as promising precursors for the production of low-cost adsorbents, because they are renewable,locally available in large quantities and inexpensive[6]. Generally the chemical modifications such as steam explosion method have done with cellulosic raw materials which render them more effective for the collection and binding of various metal ions. By applying steam explosion method the cellulose was extracted from banana stem fiber in microcrystalline form in the present study.

Fixed bed adsorption is widely used for purifying liquid mixture, especially industrial waste effluents[7].When compared to the batch, the adsorption on continuous columns presents several advantages such as simplicity in operation, faster adsorption rate and can be simply scaled up from a lab process[8]. This paper shows the strategic steps in the design and the operation of fixed bed column used for the removal of copper contaminants from synthetic solutions. The present study aims in determining the ability of NCS/SA/MC bead to remove Cu(II) from aqueous solution using fixed bed column studies and optimum conditions for adsorption by changing the bed height, flow rate and initial metal ion concentration. In addition, the kinetic models namely Thomas, Yoon-Nelson and Adam Bohart were investigated.

1. Materials

Chitosan (92% deacetylated) was purchased from India Sea Foods, Cochin, Kerala and the banana fiber was collected from local farms.The chemicals such as sodium alginate, sodium hypochlorite, oxalic acid and sodium hydroxide were purchased from Nice chemicals Pvt Ltd, India and Central Drug House Pvt Ltd, New Delhi. The crosslinking agents such as sodiumtripolyphosphate, $Cacl_2.2H_2O$ and the solvent glacial acetic acid were proccured from Finar chemicals Ltd, Ahmedabad, Nice chemicals PvtLtd, India and Sisco Research Laboratories Pvt Ltd, Mumbai respectively. All the chemicals used in the present research work were of analytical grade.

II. MATERIALS AND METHODS

2.1 Extraction of cellulose from banana fiber

The isolation of cellulose from the banana fiber was done using the steam explosion method as per the procedure reported by Bibin Mathew cherian and his coworkers[9].A combination of chemical and mechanical treatments was done with the steam exploded fibers to extract the cellulose completely. Steam explosion of the chopped lignocellulosic banana fibers (30g) with 2% NaOH (fiber to liquor ratio 1:10) solution was carried out in an autoclave at a pressure of 20 lb for a period of 1 h. The steamed alkali treated fibers were followed by sodium hypochlorite bleaching, further treated with oxalic acid and stirred mechanically well to extract the cellulose completely with different degrees of crystallinity. The photograph of the prepared four stages of fiber was represented in Fig.A

(i) (ii) (iii) (iv)

Fig.A. i) steam exploded fiber ii) bleached fiber iii) acidically treated fiber, iv) mechanically treated fiber

2.2 Preparation of nanochitosan

Nanochitosan was prepared by ionotropic gelation method using sodium tripolyphosphate as an ionic crosslinking agent as reported by Sivakami and her coworkers[10]. About 1g of chitosan was dissolved in 200ml of 2% acetic acid prepared using deionised water. The above solution was stirred well for about 20 minutes. Then to the above prepared chitosan solution, 0.8 g of sodium tripolyphosphate dissolved in 107 ml of deionized water was added drop wise with rapid stirring (30 min) to obtain an opalescent milky emulsion. It was then allowed to stand overnight to settle as suspension. After this process is over, the supernatant solution was decanted and then the thick suspension of nanochitosan settled at the bottom of the beaker was preserved in the refrigerator.

2.3 Preparation of NCS/SA/MC (2:8:1) bead

Ternary biopolymeric beads were prepared by mixing the nanochitosan, sodium alginate and microcrystalline cellulose extracted from the banana stem fiber in certain ratio. Three solutions were prepared: (i) an aqueous 2.5% nanochitosan solution; (ii) aqueous 10 wt% alginate solution and (iii) aqueous 1.25 wt% microcrystalline cellulose solution.The above prepared three solutions was mixed well at 500 rpm for about 30 minutes. This homogeneous blended mixture poured as small droplets into 0.2 M calcium chloride with the help of syringe leads to the formation of NCS/SA/MC beads.It was then allowed to stand for few hours in 0.2 M $CaCl_2$, rinsed well with distilled water to remove any excess $CaCl_2$ on the bead and then dried. A photograph of the prepared NCS/SA/MC bead was shown in Fig.B

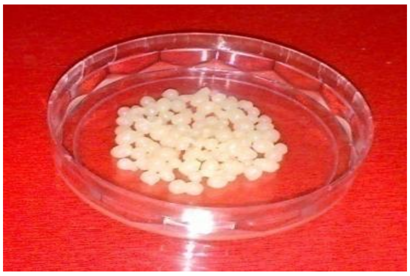

Fig.B. Photograph of NCS/SA/MC(2:8:1) bead

2.4 Fixed Bed Column Adsorption Studies

Fixed bed column studies were conducted using glass column of 2.8 cm diameter and 30 cm length. A known quantity of NCS/SA/MC bead prepared in 2:8:1 ratio was packed in the column.The metal ion (Cu(II)) solution of specific concentration was fed through the column in the down flow rate.The effluent samples were collected at specific time intervals and the heavy metals were analyzed using AAS studies. The flow to the column was continued until the effluent concentration (C) approached the influent concentration (C_o).The effect of the various factors such as the bed height (1.0 cm and 1.5 cm), flow rate (1.0ml/min and 1.5 ml/min) and initial metal ion concentration (200mg/L and 300 mg/L) on the column performance was investigated.

The loading behavior of Cu(II) to be removed from solution in a fixed bed was usually expressed in term of C_t/C_o where (C_t = effluent Cu(II) ion concentration and C_o = influent Cu (II) ion concentration in mg/l). C_t/C_o is then plotted against time in order to obtain breakthrough curve. Total adsorbed metal quantity ($q_{total,}$ mg) in the column for a given feed concentration and flow rate is calculated as follows (equation-(1)):

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=total} C_{ad}.dt \qquad \text{-------(1)}$$

Total amount of metal ion sent to column (m_{total}) is calculated as follows (equation-(2)):

$$m_{total} = \frac{C_0\,Q\,t_{total}}{1000} \qquad \text{------- (2)}$$

Total removal is calculated as follows (equation-(3)):

$$\text{Total Removal (\%)} = \frac{q_{total}}{m_{total}}\ x\ 100 \qquad \text{-------(3)}$$

The breakthrough capacity (q_b) and the volume of effluent solution (V_{eff}) treated was determined using the following equation (equation-(4) and equation-(5))

$$q_b = \frac{t_b Q C_o}{m} \qquad \text{-------(4)}$$

$$V_{eff} = Qt_{total} \qquad \text{-------(5)}$$

where C_o = initial influent concentration of solute (mg/l), q_b = breakthrough adsorption capacity (mg/g), t_b = breakthrough time (min), Q = volumetric flow rate (ml/min), m = mass of adsorbent used (g), V_{eff} = volume of effluent (L), t_{total} = total flow time respectively.

2.5 Column Adsorption kinetic Models

Various kinetic models have been developed to predict the dynamic behavior of the column.

2.5.1 Thomas Model

Thomas model assumes no axial dispersion and Langmuir adsorption-desorption kinetics.This model is used to calculate the adsorption rate constant and the solid phase concentration of the metal ion on the adsorbent from the continuous mode studies [11]. The linearized form of the Thomas model can be expressed in equation-(6):

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{TH} q_o X}{Q} - \frac{k_{TH} C_o}{Q} V_{eff} \qquad \text{--------- (6)}$$

where C_t and C_o the effluent and influent metal ion concentration at time t (mg/L), k_{TH} is the thomas rate constant (ml min^{-1} mg^{-1}), q_o is the maximum adsorption capacity (mg g^{-1}), X is the amount of adsorbent in the column (g), V_{eff} is throughput volume (ml) and Q is the flow rate (ml min^{-1}). The kinetic coefficient k_{TH}, the equilibrium uptake per gram of the adsorbent q_o can be determined from the slope and intercept of plot of $\ln(C_o/C_t -1)$ against effluent volume (V_{eff}).

2.5.2 Yoon Nelson Model

The Yoon–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[12].The linearized form of the Yoon-Nelson model is given below (equation-(7)):

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN}\, t - \tau k_{YN} \qquad \text{--------(7)}$$

where, k_{YN} is Yoon and Nelson rate constant (min^{-1}), C_t and C_o is the effluent and inlet solute concentrations, τ is the time required for 50% adsorbate breakthrough (min) and t is the time (min). A plot of ln (C_t/C_o-C_t) versus t gives a straight line with slope of k_{YN} and intercept of - $\tau.k_{YN}$. With the help of it the k_{YN} and τ values were calculated.

2.5.3 Adams Bohart model

Adams-Bohart model is based on the assumption that the adsorption rate is proportional to the fraction of adsorption capacity that still remains on the surface of the adsorbent [13]. The Adam-Bohart model is used for the description of the initial part of the breakthrough curve. The Adam-Bohart expression is given as follows (equation-(8)):

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB} C_o t - k_{AB} N_o \frac{Z}{F} \qquad \text{--------(8)}$$

where C_t and C_o are the effluent and influent concentrations (mg L^{-1}) at time t and zero, k_{AB} is the kinetic constant (ml mg^{-1} min^{-1}), t is time (min); N_0 is the saturation concentration (mg L^{-1}), Z is the bed depth of column (cm), F is the superficial velocity of influent solution calculated by dividing the flow rate by the column section area (cm/min). The parameters describing the characteristic operations of the column (k_{AB} and N_0) were determined from intercept and slope of linear plot of ln (C_t/C_o) against time (t) respectively.

The proposed mechanism of binding of Cu(II) onto the nanochitosan/sodium alginate/microcrystalline cellulose bead was represented in Fig.C.

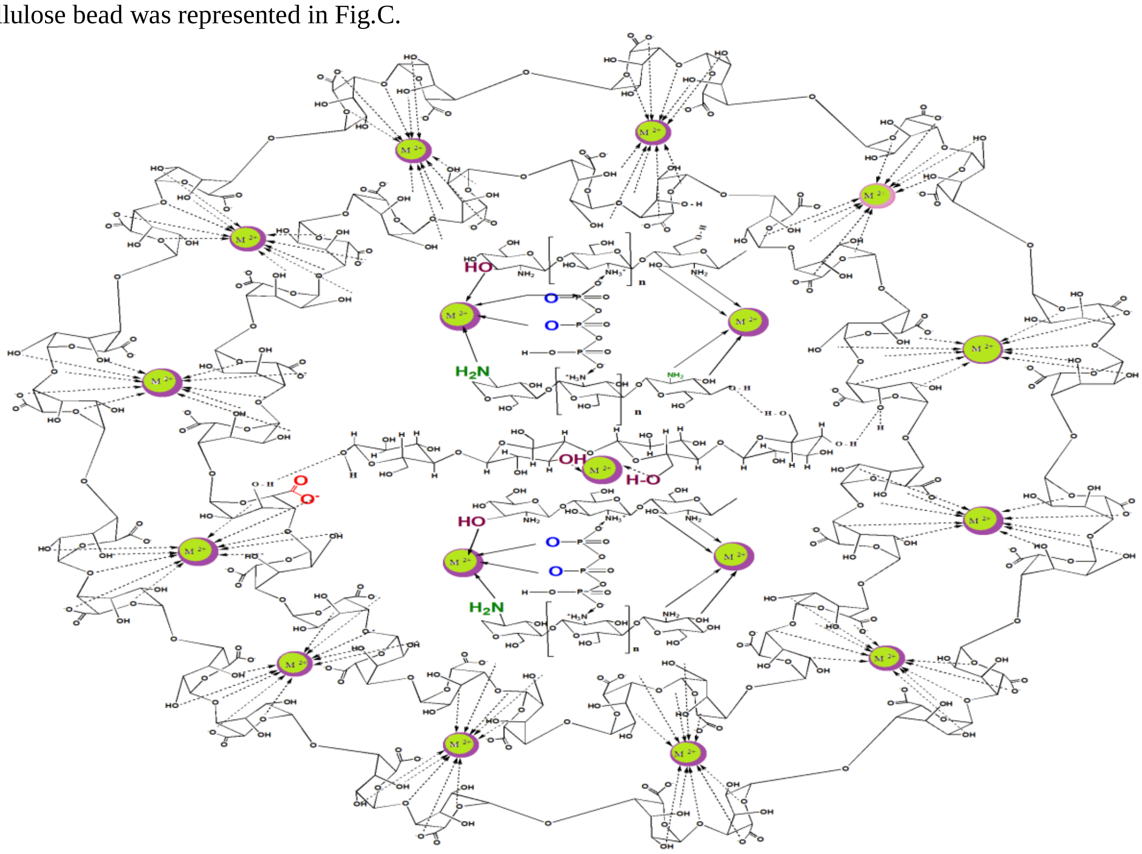

Fig.C. Proposed mechanism of binding of Cu(II) onto the nanochitosan/sodium alginate/microcrystalline cellulose bead

III. Results and discussion

3.1 Optimization of Column Parameters

3.1.1 Effect of bed height

The removal of Cu(II) at different bed heights (Z:1.0 cm and 1.5 cm) was studied and the breakthrough curves obtained at different bed heights at constant flow rate (Q:1.5ml/min) and initial metal ion (Cu(II)) concentration (C_o:200mg/L) was shown in Fig.1 and TABLE-1.

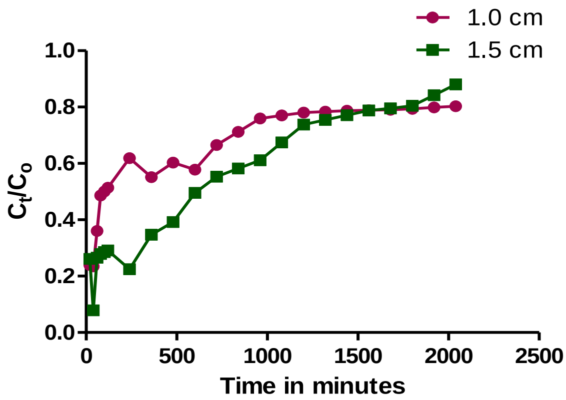

Fig.1. Effect of bed height

TABLE-1: Parameters of the fixed bed column at different bed heights

Z (cm)	Q (mL/min)	C_o (mg/L)	t_b (min)	t_{total} (min)	Total removal (%)
1.0	1.5	200	40	840	39.41
1.5	1.5	200	60	1200	50.89

From the Fig.1 and TABLE-1, it is evident that the breakthrough time, removal efficiency and saturation time increases with increase in bed height. The observed increase in the removal efficiency with increased bed height was attributed to the higher number of binding sites and the increased volume of effluent[14]. These above observations suggest that the bed height of 1.5 cm offered optimum breakthrough curves and hence further experiments were carried out at this bed height.

3.1.2 Effect of flow rate

The effect of flow rate for the adsorption of copper (II) onto NCS/SA/MC bead at flow rates of 1.0 ml/min and 1.5 ml/min at an influent concentration of 200 mg/L and bed height of 1.5 cm was shown in Fig.2 and TABLE-2.

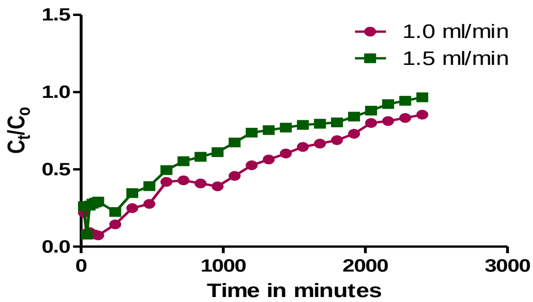

Fig.2. Effect of flow rate

TABLE-2: Parameters of the fixed bed column at different flow rates

Z (cm)	Q (ml/min)	C_o (mg/L)	t_b (min)	t_{total} (min)	Total removal (%)
1.5	**1.0**	200	80	2040	52.50
1.5	**1.5**	200	60	1200	50.89

The above obtained breakthrough curves indicate that the column performed well with higher removal efficiency, longer breakthrough time and longer saturation time at lower flow rate (1.0 ml/min) when compared to the higher flow rate (1.5ml/min). This may be due to the fact at slower flow rate the residence time of metal ions in column with the adsorbent increases and as a result the metal ions can have more time to diffuse into the pores of NCS/SA/MC bead through intraparticle diffusion resulting in longer breakthrough time, saturation time and higher removal efficiency[15] whereas at higher flow rate the contact time of the metal ions with the adsorbent in the column is not enough to reach adsorption equilibrium and hence the metal ion (Cu(II)) solution leaves the column before equilibrium occurs. This causes a reduction in the removal efficiency, breakthrough time and saturation time.Based on the above obtained results it was identified that the optimal flow rate was found to be 1.0 ml/min for Cu(II) removal from aqueous solution.

3.1.3 Effect of initial metal ion concentration

At an optimum bed height (1.5cm) and flow rate (1.0ml/min) the effect of initial concentration of Cu(II) ions on their adsorption process was studied and the breakthrough curves obtained was shown in Fig.3 and TABLE-3.

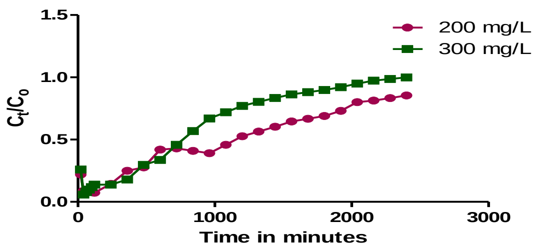

Fig.3. Effect of initial metal ion concentration

TABLE-3: Parameters of the fixed bed column at different metal ion concentration

Z (cm)	Q (mL/min)	C_o (mg/L)	t_b (min)	t_{total} (min)	Total removal (%)
1.5	1.0	**200**	80	2040	52.50
1.5	1.5	**300**	60	1920	40.79

From the observed results of Fig.3 and TABLE-3, it can be deduced that the removal efficiency, breakthrough time and the column exhaustion time decreased with the increase in initial metal ion concentration.The increased removal efficiency at lower metal ion concentration might be due to the availability of sufficient active sites for the adsorption of the metal ions. At higher metal ion concentration the number of metal ions is relatively higher compared to the availability of adsorption sites,most of the metal ions left unadsorbed and hence the % removal of metal ions shows a decrease[16].

3.2 Determination of kinetic constants

3.2.1 Thomas Kinetic Model

Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting. Fig.(4)-(6) represents the linear plot of Thomas model with experimental data at different bed heights (1.0 cm, 1.5 cm), flow rates (1ml/min, 1.5 ml/min) and initial metal ion concentrations (200mg/L, 300mg/L) for NCS/SA/MC bead. TABLE –4 represents the calculated values of Thomas model parameters and the R^2 at different conditions using linear regression analysis for NCS/SA/MC bead.

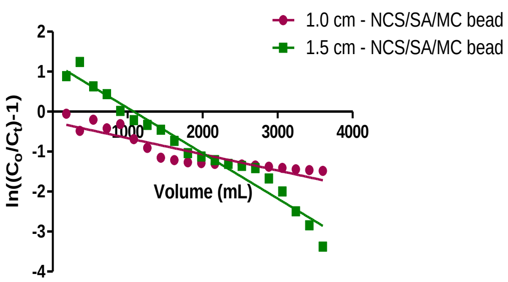

Fig.4. Effect of bed height- Thomas kinetic plot

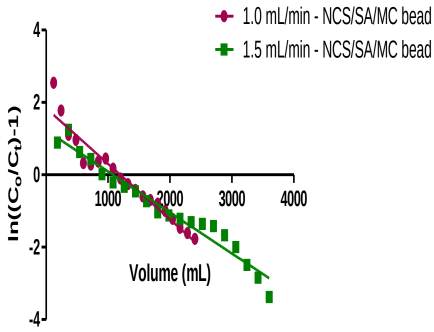

Fig. 5. Effect of flow rate- Thomas kinetic plot

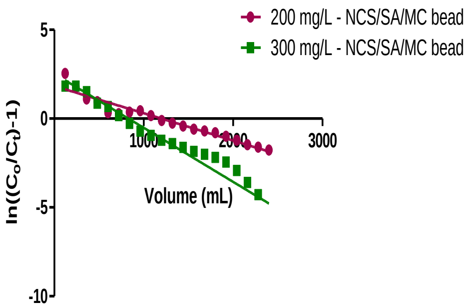

Fig. 6. Effect of initial metal ion concentration- Thomas kinetic plot

TABLE-4: Thomas model parameters at different conditions

Co (mg/L)	Z (cm)	Q (ml/ min)	Thomson Constant		R^2
			k_{TH} (ml/min/mg) ($x10^{-6}$)	q_0(mg/g) ($x10^4$)	
200	**1.0**	1.5	3.038	5.7270	0.8221
200	**1.5**	1.5	8.505	5.4012	0.9603
200	1.5	**1.0**	7.680	5.3711	0.9339
200	1.5	**1.5**	8.505	5.4012	0.9603
200	1.5	1.0	7.680	5.3711	0.9339
300	1.5	1.0	7.667	8.2337	0.8876

The results of k_{TH}, R^2 and q_o presented in TABLE-(4) obtained from Fig.(4)-(6) reveals that the maximum adsorption capacity, q_o increased with increase in flow rate and initial ion concentration but decreased with increase in bed height. The observed increase in q_o with increase in flow rate was attributed to the availability of active sites of adsorbent by the numerous adsorbate molecules present in higher flow of solution [17].The Thomas rate constant, k_{TH} increased with increase in bed height, flow rate but decreased with increase in metal ion concentration.

3.2.2 Yoon Nelson kinetic model

The values of Yoon nelson rate constant (k_{YN}) and τ obtained for all the breakthrough curves including correlation coefficients calculated from the slope and intercept of plot of ln (C_t/C_o-C_t) versus t (Fig- (7)-(9)) was represented in TABLE-5.

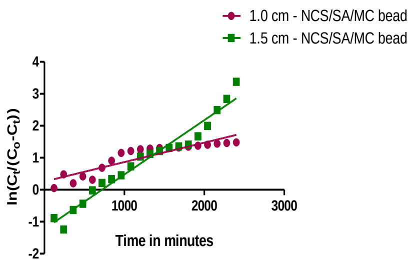

Fig.7. Effect of bed height- Yoon Nelson kinetic plot

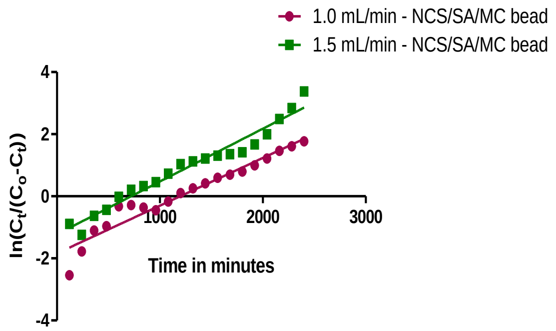

Fig.8. Effect of flow rate- Yoon Nelson kinetic plot

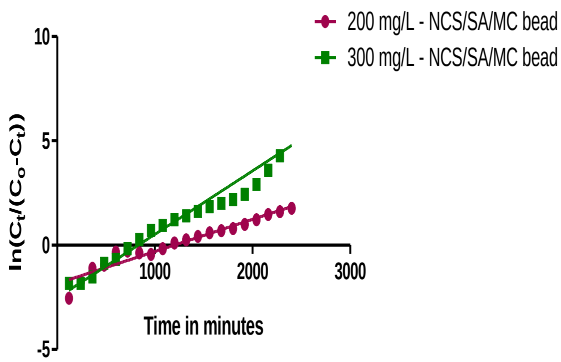

Fig.9.Effect of initial metal ion conc- Yoon Nelson kinetic plot

TABLE- 5: Yoon Nelson model parameters at different conditions

C_o (mg/L)	Z (cm)	Q (ml/min)	Yoon Nelson Constant		R^2
			k_{YN} (ml/min/ mg)(X 10^{-3})	□ (min)	
200	**1.0**	1.5	0.608	423.893	0.8221
200	**1.5**	1.5	1.700	720.588	0.9603
200	1.5	**1.0**	1.536	1196.615	0.9339
200	1.5	**1.5**	1.700	720.588	0.9603
200	1.5	1.0	1.536	1196.615	0.9339
300	1.5	1.0	3.043	829.773	0.8876

The above obtained results indicate that the k_{YN} increased with increased metal ion concentration, flow rate and bed height whereas the time required for 50% breakthrough τ decreased with increase in flow rate, initial metal ion conc and increased with increase in bed height. Because of less residence time the value of τ decreased with increased flow rate[18]. The decreased value of τ with increased flow rate and initial Cu(II) ion conc might be due to attainment of saturation of column quickly. The increased τ value with the increase in bed height was due to slower saturation of column.

3.2.3 Adam Bohart model

The Adam-Bohart model is used for the description of the initial part of the breakthrough curve. Fig.(10)-(12) and TABLE-6 represents the linear plot and parameters of Adam Bohart model with experimental data at different bed heights, flow rates and initial metal ion concentrations for NCS/SA/MC bead (copper (II)).

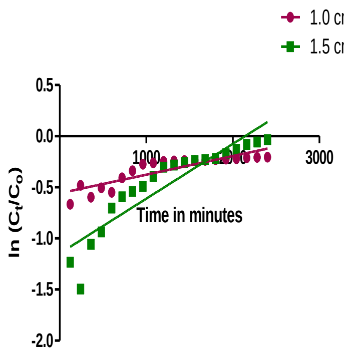

Fig.10. Effect of bed height- Adam Bohart kinetic plot

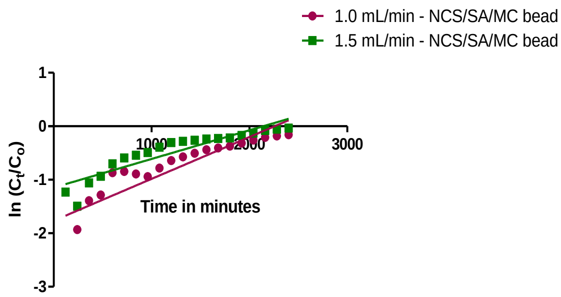

Fig.11. Effect of flow rate- Adam Bohart kinetic plot

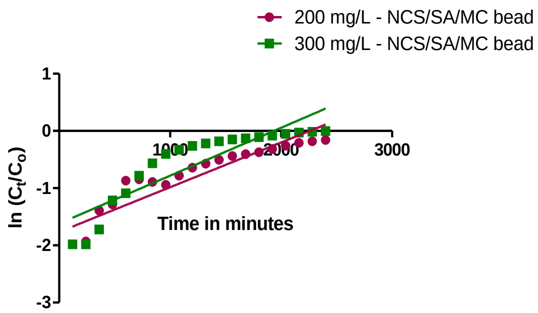

Fig.12. Effect of initial metal ion conc- Adam Bohart kinetic plot

TABLE-6: Adam Bohart model parameters at different conditions

C_o (mg/L)	Z (cm)	Q (ml/min)	Adam Bohart Constant		R^2
			k_{AB}(L/min/mg) (x 10^{-6})	N_o(mg/L) (X10^4)	
200	**1.0**	1.5	0.910	10.473	0.7595
200	**1.5**	1.5	2.678	4.8726	0.8384
200	1.5	**1.0**	3.910	3.4256	0.7791
200	1.5	**1.5**	2.678	4.8726	0.8384
200	1.5	1.0	3.910	3.4256	0.7791
300	1.5	1.0	2.791	4.3995	0.7874

From TABLE-6 , it can be seen that the values of N_o increased with increase in flow rate and metal ion concentration but decreased with increase in bed height. The values of k_{AB} decreased with increase in initial metal ion concentration as well as the flow rate. This showed that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in column[19].

IV. CONCLUSION

Based on the analysis conducted in this study, it was concluded that the NCS/SA/MC bead can be efficiently utilized as an adsorbent in a continuous column for removing Cu(II) from aqueous solution. The main outcome of this column study is that an optimal flow rate of 1.0 ml/min with a packing height of 1.5cm and C_o = 200 mg/L was found to be the most effective combination for removing maximum amount of Cu(II) from the aqueous solution. Finally based on the higher correlation coefficient values (R^2>0.84) it was concluded that the experimental data showed a better fit to the Thomas and Yoon-Nelson model and hence these models can be used to describe the behavior of the adsorption process.

REFERENCES

[1] S.H.Key, H.J.Jae and K.L.Won, Fixed Bed Adsorption for Bulk Component System, *Chemical Engineering Science,50 (5),*1995, 813-825 .

[2] Jibesh Datta and Umesh Mishra, Cadmium Removal by Column Study from Aqueous Environment Using Tea Factory Waste as Adsorbent, *Journal of chemical biological and physical sciences, 4(3),* 2014, 2727-2741.

[3] J.Virkutyte, E.Hullebusch, M.Sillanpee, P. Lens,Copper and trace element fractionation in electrokinetically treated anaerobic granular sludge, *Environmental Pollution, 138 (3),* 2005, 517–528.

[4] Iman Mobasherpour, Esmail Salahi and Ali Asjodi, Batch and Fixed-Bed Column Performance of Red Mud Adsorbents for Pb(II) Removal, *Canadian chemical transactions, 2 (1),*2014, 83-96.

[5] Takeshi Gotoh, Keiei Matsushima,Ken-Ichi Kikuchi, Preparation of alginate–chitosan hybrid gel beads and adsorption of divalent metal ions, *Chemosphere, 55,* 2004, 135–140.

[6] C. C. O. Alves, P. D. Rocha, A. S. Franca and L. S. Oliveira, Preparation and characterization of activated carbons based on lignocellulosic residues, *Advanced Material Research, 856,* 2013, 69-73.

[7] Z.R. Yelebe, B. Z. Yelebe and R.J. Samuel, Design of fixed bed column for the removal of metal contaminants from industrial wastewater, *Journal of Engineering and Applied sciences, 5(2)*, 2013, 68-77.

[8] R. W. Gaikwad, Removal of copper (II) ions from Acid Mine Drainage effluents using Psidium Guava leaves powder, *International Journal of Advanced Research, 1(10),* 2013, 944-950.

[9] Bibin Mathew Cherian , Laly A Pothan Tham Nguyen Chung , Gunter Menning , Kottaisamy and Sabu Thomas, A novel method for the synthesis of cellulose nanofibril whiskers from banana fibers and characterization, *Journal of agricultural and food chemistry, 56(14),* 2008, 5617-5627.

[10] M.S.Sivakami, T. Gomathi, J.Venkatesan, H.S.Jeong, S.K. Kim and P.N. Sudha, Preparation and characterization of nanochitosan for treatment wastewaters, *International Journal of biological macromolecules, 57,* 2013, 204– 212.

[11] S. Tamilselvi and M.Asaithambi, Adsorptive removal of methylene blue dye using a packed bed column prepared from novel adsorbent, International Journal of science and technology management, 4(3), 2015, 83-92 .

[12] A.A. Ahmad and B.H.Hameed, Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste, Journal of Hazardous Materials,175(1-3), 2010, 298–303.

[13] M. Lehmann, A.I. Zouboulis, K.A. Matis, Modelling the sorption of metals from aqueous solutions on goethite fixed-beds, *Environmental Pollution, 113(2),* 2001,121-128.

[14] R. Lakshmipathy and N. C. Sarada, A fixed bed column study for the removal of Pb(II)ions by watermelon rind, *Environmental Science Water Research Technology, 1,* 2015, 244-250.

[15] G.Yan and T.Viraraghavan, Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass, *Bioresource Technology, 78(3),* 2001, 243-249.

[16] Hadeel Ali Al-Husseiny, Adsorption of methylene blue dye using low cost adsorbent of sawdust: Batch and continues studies, J. *Babylon University/Engineering Sciences, 22(2),* 2014, 296-310.

[17] Naima Azouaou, Zahra Sadaoui, Hassiba Mokaddem, Removal of Lead from Aqueous Solution onto Untreated Coffee Grounds: a Fixed-bed Column Study, *Chemical Engineering transactions, 38,* 2014, 151-156.

[18] Zahra Saadi, Reyhane Saadi and Reza Fazaeli, Fixed-bed adsorption of Pb (II) adsorption from aqueous solution using nanostructured γ-alumina, *Journal of nanostructuyre in chemistry, 3(48),* 2013, 1-8.

[19] Z.Aksu and F.Gonen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, *Process Biochemistry, 39(5),* 2004, 599–613.