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Kinetic Modeling of Heavy Metals Adsorption on fixed bed Column

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ABSTRACT: The adsorption of lead (11) and copper (11) in a fixed bed column using activated carbon prepared from nipa palm nut was investigated. Thomas model and Yoon and Nelson kinetic models were used to analyze the column performance. The rate constant for Thomas model increased with increase in flow rate and initial ion concentration but remained constant at varying bed height. Adsorption capacity for the adsorption of copper (11) obtained from Thomas model ranged from 3.417 to 17.224 mg/l for Thomas model and from 3.02 to 11.92mg/l for Yoon and Nelson model. Also the adsorption capacity for lead (11) adsorption calculated from Thomas model ranged from 6.937 to 75.59 mg/l and from 12.10 to 47.24 mg/l for Yoon and Nelson model. The maximum adsorption capacity increased with increase in flow rate and initial ion concentration but decreased with increase in bed height. For Yoon and Nelson model, the rate constant increased with increase in flow rate, initial ion concentration and bed height. The time required for 50% breakthrough decreased with increase in flow rate, bed height and initial ion concentration. The kinetic data fitted well to both models. The comparison of the experimental breakthrough curves to the breakthrough profiles calculated by Yoon and Nelson method showed a satisfactory fit for activated carbon prepared from nipa palm nut.

Key words: Kinetics, modeling, Adsorption, heavy metals, fixed bed column

INTRODUCTION

With the rapid development of chemical and petroleum processing industries in Nigeria, there is an increase in the amount and the variety of chemicals that are discharged into waters. Wastewater from various industries and municipal corporations are discharged into ground and surface water, making it unfit for human and animal consumption. Some of the organic and inorganic compounds, when present in water, are toxic, carcinogenic, and mutagenic, and they cause several ailments in humans (Roque-Malherbe, 2007, Bansal and Goyal, 2005). Heavy metal ions are described as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity (Volesky and Holan, 1995; Nasrabadi *et al.,* 2010; Haruna *et al.,* 2011; Serbaji *et al.,* 2012; Ogundiran *et al.,* 2012; Yu *et al.,* 2011; Kargar *et al.,* 2012;; Mzoughi and Chouba, 2012; Ghaderi *et al.,* 2012). These heavy metals are not biodegradable and their presence in waters leads to bioaccumulation in living organisms causing health problems in animals, plants, and human beings (Ong *et al.,* 2007; Alimohammad Kalhori *et al.,* 2012; Ashraf *et al.,* 2012; Okuku and Peter, 2012; Mhadhbi *et al.,* 2012; Divis *et al.,* 2012). Lead is a pollutant that is present in drinking water and in air. Lead is known to cause mental retardations, reduces haemoglobin production necessary for oxygen transport and it interferes with normal cellular metabolism (Qaiser *et al.,* 2007). Copper is metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys (Antonijevic and Petrovic, 2008). Adsorption onto activated carbon has been found to be better than other methods of wastewater treatment because of its capability for adsorbing a broad range of different types of adsorbates efficiently, and its simplicity of design (Ahmad *et al.,* 2006; Markovska *et al.,* 2006). Many researchers have studied cheaper substitutes, which are relatively inexpensive, and are at the same time endowed with reasonable adsorptive capacity. These studies include the use of coal (Mohan *et al.,* 2002), fly ash (Mohan *et al.,* 2002; Nollet *et al.,* 2003; Gupta *etal.,* 2003; Ricou *etal.,* 2001, Gupta and Ali, 2004), etc. The study of sorption kinetics in wastewater treatment is important since it provides valuable insights into the reaction pathways and mechanism of adsorption process (Mincera *etal.,* 2008; Maximova and Koumanova, 2008). In order to examine

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the mechanism of adsorption process, a suitable kinetic model is needed to analyse the rate data (Ozacar, 2003). Two models (Thomas model and Yoon and Nelson model) were used to analyze the column performance for the removal of lead (11) and copper (11) from aqueous solution using activated carbon prepared from nipa palm nut (NPN). The Thomas model is also referred to as the bed-depth-service-time (BDST) model (Kavak and Öztürk, 2004). Yoon and Nelson model is based on the assumption 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 (Kavak and Őztürk, 2004). This work provides data for the design of wastewater and water treatment equipment.

MATERIALS & METHOD

Nipa palm nuts were obtained from Nkpogu village, Rivers state, Nigeria. The palm nuts were washed with deionized water, dried in the sun, ground into fine particles and sieved to a particle size of 300μm. 200g of sample was impregnated with concentrated orthophosphoric acid at the acid/precursor ratio of 2:1 (wt basis). The impregnated sample was dried in an oven at 120^{0}C for 24hrs. The dried sample was carbonized in a Muffle furnace for 1hr at 500^{0}C. After cooling to the ambient temperature, the sample was washed with de-ionized water several times until pH 6-7, filtered with Whatman No.1 filter paper and then dried in the oven at 110^{0}C for 8hours. The sample was crushed and passed through different sieve sizes and then stored in a tight bottle ready for use.

The pH of the carbon was determined using standard test of ASTM D 3838-80 (ASTM, 1996). Moisture content of activated carbon and raw materials was determined using ASTM D 2867-91 (1991).The bulk density of the activated carbon was determined according to the tamping procedure by Ahmedna et al (1997). The volatile content was determined by weighing 1.0g of sample and placing it in a partially closed crucible of known weight. It was then heated in a muffle furnace at 900^{0}C for 10mins.The percentage fixed carbon was determined as100 – (Moisture content + ash content + volatile matter). The iodine number was determined based on ASTM D 4607-86 (1986) by using the sodium thiosulphate volumetric method The specific surface area of the activated carbon was estimated using Sear's method (Al-Qadah and Shawabkah, 2009 and Alzaydien, 2009) by agitating 1.5g of the activated carbon samples in 100ml of diluted hydrochloric acid at a pH = 3. Then a 30g of sodium chloride was added while stirring the suspension and then the volume was made up to 150ml with deionized water. The solution was titrated with 0.1N NaOH to raise the pH from 4 to 9 and the volume, V recorded. The surface area according to this method was calculated as S = 32V – 25. Where, S = surface area of the activated carbon, V = volume of sodium hydroxide required to raise the pH of the sample from 4 to 9.

The chemicals used were lead nitrate salt ($Pb(NO_3)_2$), copper sulphate ($CuSO_4$) and de-ionized water. The reagents were of high grade. The samples ($Pb(NO_3)_2$ and ($CuSO_4$) were dried in an oven for 2hrs at 105^{0}C to remove moisture. The adsorbates were produced by dissolving 1.6g and 2.51g of $Pb(NO_3)_2$ and $CuSO_4$ respectively in 1000ml of de-ionized water separately to get the stock solution of 1000g/L.

A glass adsorption column of 30mm internal diameter and length of 300mm was used to perform fixed bed column studies. The granulated activated carbon having 0.425mm to 0.600mm particle size range was used. The activated carbon was packed in the column with a layer of glass wool at the bottom. Bed height of 50mm, 100mm and 150mm was used. The metal solution was introduced into the column by gravitational flow. The first tank delivers the solution to the second tank at a constant flow rate. The second tank is equipped with a pipe to help maintain a constant solution level in the tank in order to maintain a constant flow rate of the solution being delivered to the column. The second flow controller was used to regulate the flow rate. Three flow rates (5, 7.5 and 10ml/min) were used with initial ion concentrations of 50, 100 and 150mg/l. The adsorption study was performed at 30^{0}C and pH of 6 and 7 for lead (11) and copper (11) respectively. The effluent samples were collected at specified intervals and analyzed for the residual ion concentration using atomic adsorption spectrophotometer at 217nm for Pb^{2+} and 324.8nm for Cu^{2+}. Column studies were terminated when the column reached exhaustion. The schematic diagram of the mini adsorption column used is shown in Fig. 1.

RESULTS & DISCUSSION

Characteristics of activated carbon derived from nipa palm nut

The physico-chemical characteristics of activated carbon are shown in Table 1.

Thomas model and Yoon and Nelson kinetic models were used to analyze the column performance. Thomas model has been used by many researchers to study packed bed adsorption kinetics (Kavak and Öztürk, 2004; Baek etal., 2007 and Sivakumar and Palanisamy, 2009). The linearized form of the Thomas model is described by equation (1) (Kavak and Öztürk, 2004).

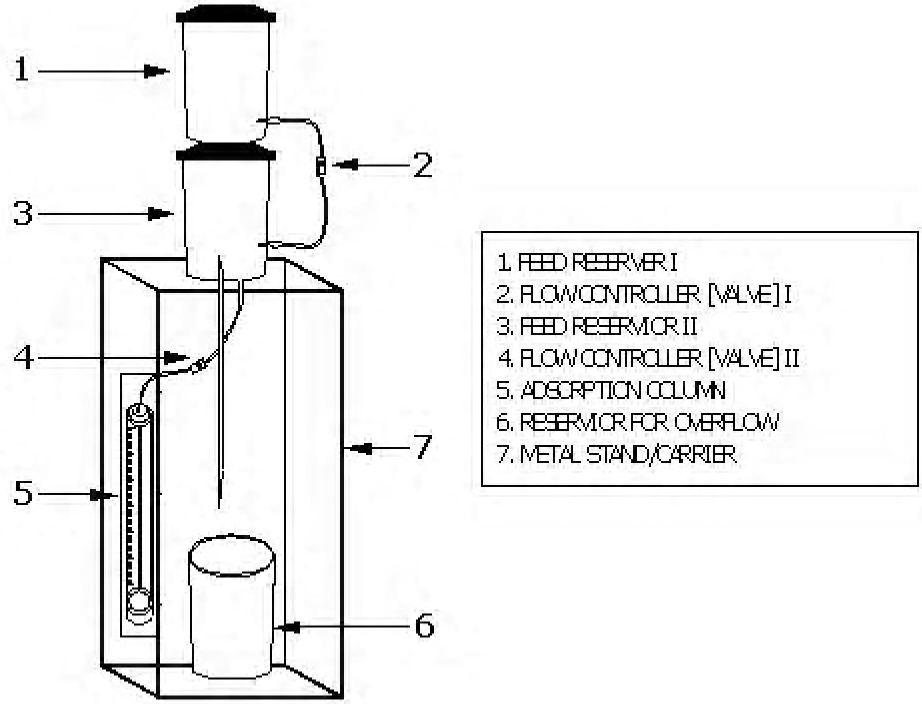

Table 1. The physico-chemical characteristics of activated carbon prepared from NPN

Properties	Values
pH	6.9
Bulk density, g/cm^3	0.53
Iodine number, mg/g	815.62
Moisture content, %	4.80
Volatile matter, %	24.60
Ash content, %	3.88
Fixed carbon, %	71.52
Surface Area, m^2/g	871.22

$$In\left(\frac{C_o}{C_e}-1\right)=\frac{K_T q_o M}{Q}-\frac{K_T C_o}{Q}V \qquad (1)$$

Where C_e, C_o = the effluent and inlet solute concentrations (mg/l), q_o = the maximum adsorption capacity (mg/g), M = the total mass of the adsorbent (g), Q = volumetric flow rate (ml/min), V = the throughput volume (ml) and K_T = the Thomas rate constant (ml/min/mg). The kinetic coefficient, K_T and the adsorption capacity of the bed, q_o were determined from the plot of In [(C_o/C_e)-1] against V at a given flow rate (Fig.s 2, 3, 4, 5, 6, 7). The results of K_{-T}, R^2 and q_o are given in Tables 2 and 3. The values of K_T obtained in this work are similar to the ones obtained by Sivakumar and Palanisamy (2009). High values of regression coefficients were determined indicating that the kinetic data conformed well to Thomas model in contrast with the report of Sivakumar and Palamisamy (2009) but in agreement with the results obtained by Baek et al (2007). Thomas rate constant, K_T increased with increase in flow rate and initial ion concentration but remained constant at varying bed height. The maximum adsorption capacity, q_o increased with increase in flow rate and initial ion concentration but decreased with increase in bed height.

These authors used Yoon and Nelson model in the study of column adsorption kinetics (Tsai *et al.*, 1999; Kavak and Öztürk, 2004; Sivakumar and Palanisamy, 2009). The linear form of Yoon and Nelson model is represented as (Aksu and Gönen, 2004 and Sivakumar and Palanisamy, 2009).

$$In\left(\frac{C_e}{C_o-C_e}\right)=K_{YN}t-\tau\cdot K_{YN} \qquad (2)$$

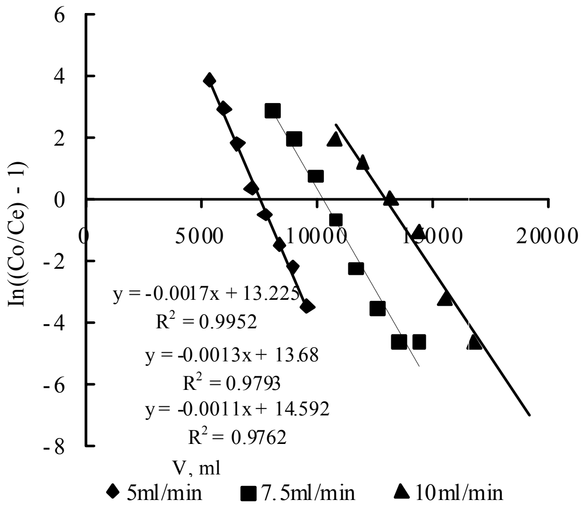

Fig. 2. Thomas kinetic plot for the adsorption of Pb^{2+} on NPN: Effect of flow rate

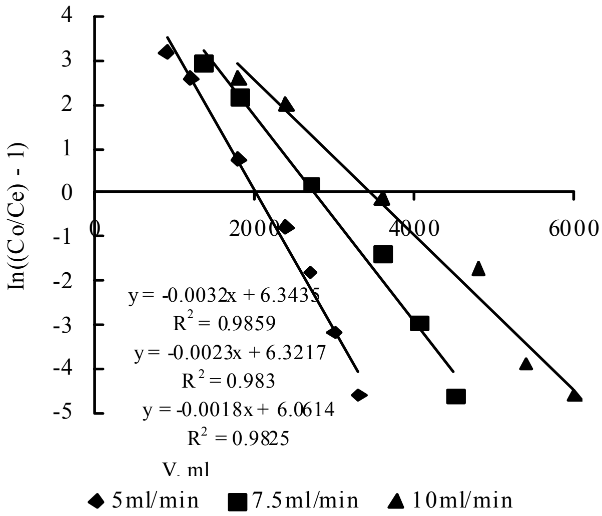

Fig. 3. Thomas kinetic plot for the adsorption of Cu^{2+} on NPN: Effect of flow rate

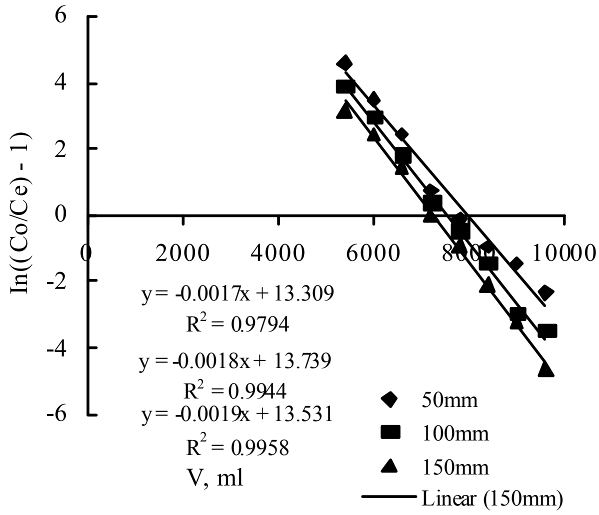

Fig. 4. Thomas kinetic plot for the adsorption of Pb^{2+} on NPN: Effect of bed height

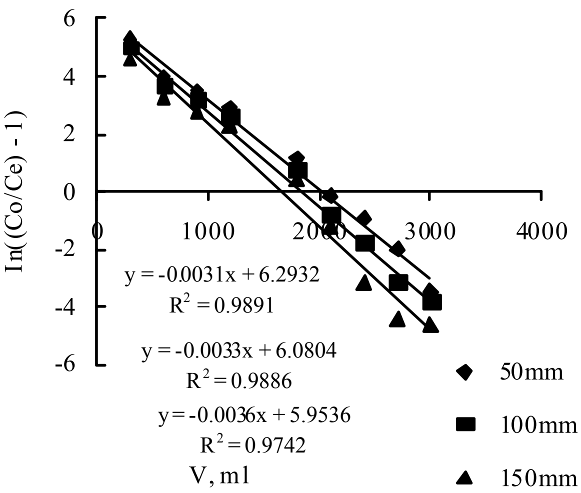

Fig. 5. Thomas kinetic plot for the adsorption of Cu^{2+} on NPN: Effect of bed height

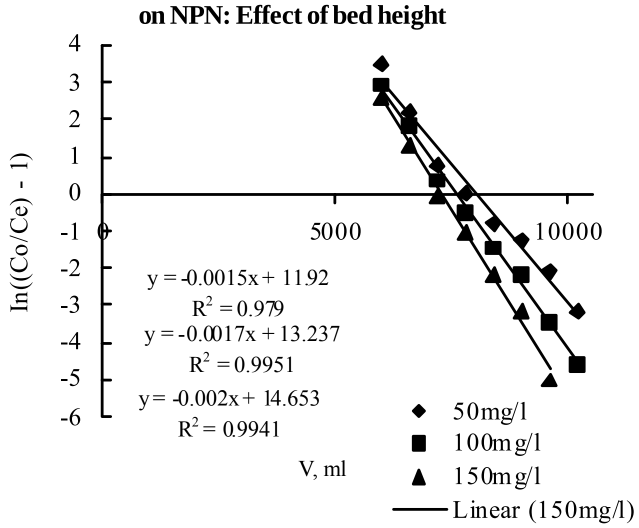

Fig. 6. Thomas kinetic plot for the adsorption of Pb^{2+} on NPN: Effect of initial ion concentration

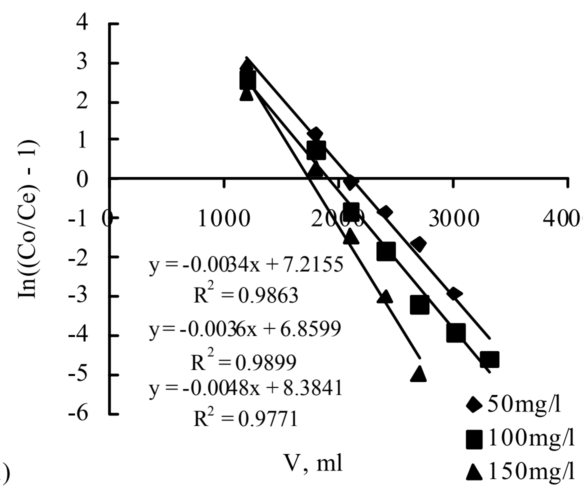

Fig. 7. Thomas kinetic plot for the adsorption of Cu^{2+} on NPN: Effect of initial ion concentration

Where, K_{YN} is Yoon and Nelson rate constant, C_e, C_o is the effluent and inlet solute concentrations, τ is the time required for 50% adsorbate breakthrough (min) and t is the breakthrough (sampling) time (min).

A plot of In $C_e/(C_o-C_e)$ versus t gives a straight line with slope of K_{YN}, and intercept of $-\tau.K_{YN}$ (Figs 8, 9, 10, 11, 12, 13). The values of K_{YN}, τ and adsorption capacity, q_o obtained are listed in Table 2 and 3. Both K_{YN} and τ are dependent on the initial ion concentration (Tsai *et al.,* 1999). The results show that K_{YN} increased with increased ion concentration, whereas the 50% breakthrough time, τ decreased. Also, adsorption capacity, q_o decreased with increase in bed height and increased with increase in flow rate and initial ion concentration. This is due to the fact that increase in initial ion concentration increases the competition between adsorbate molecules for the adsorption site, which ultimately results in increased uptake rate (Sivakumar and Palanisamy, 2009). The rate constant increased with increase in flow rate and bed height. The time required for 50% breakthrough τ decreased with increase in flow rate and increase in initial ion concentration. High values of correlation coefficients indicate that Yoon and Nelson model fitted well to the experimental data. This is in agreement with the results obtained by Tsai, et al. (1999).

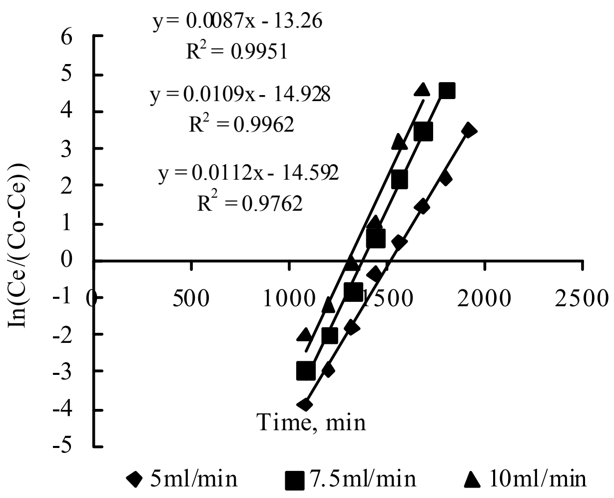

Fig. 8. Yoon and Nelson kinetic plot for the adsorption of Pb^{2+} on NPN: Effect of flow rate

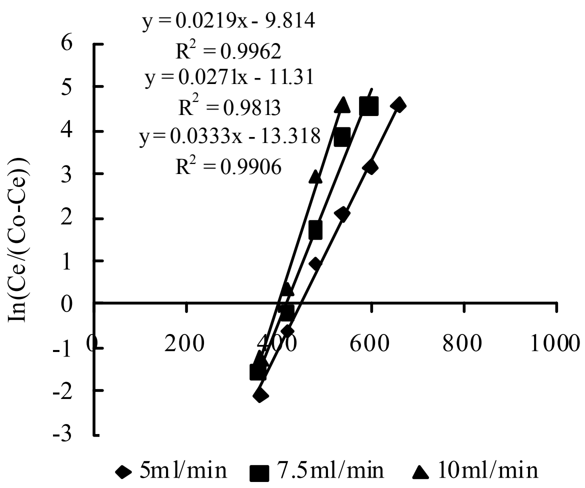

Fig. 9. Yoon and Nelson kinetic plot for the adsorption of Cu^{2+} on NPN: Effect of flow rate

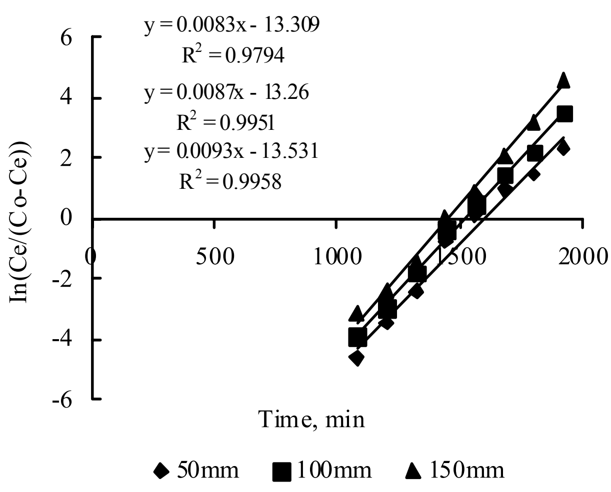

Fig.10. Yoon and Nelson kinetic plot for the adsorption of Pb^{2+} on NPN: Effect of bed height

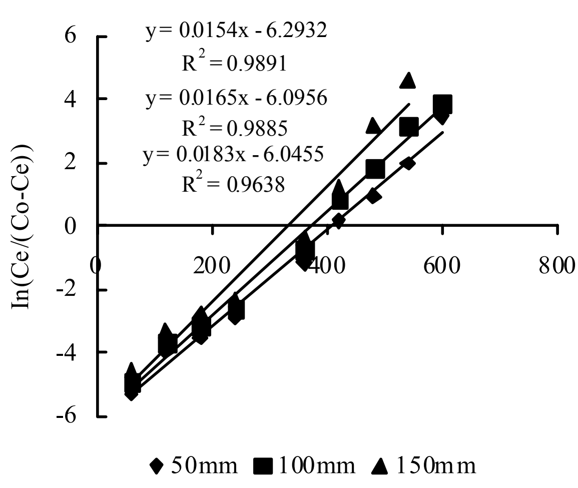

Fig.11. Yoon and Nelson kinetic plot for the adsorption of Cu^{2+} on NPN: Effect of bed height

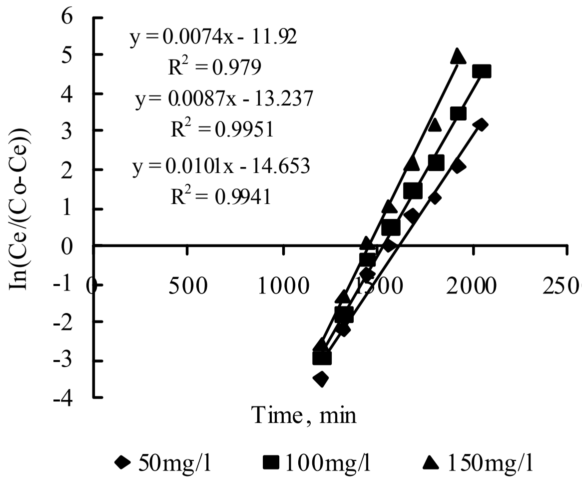

Fig.12. Yoon and Nelson kinetic plot for the adsorption of Pb^{2+} on NPN: Effect of initial ion concentration

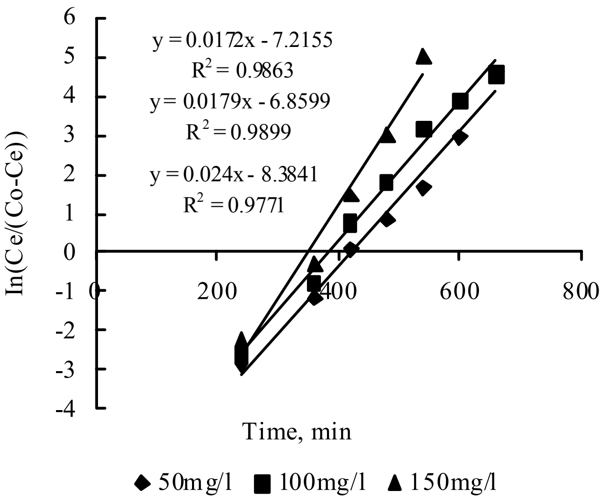

Fig. 13. Yoon and Nelson kinetic plot for the adsorption of Cu^{2+} on NPN: Effect of initial ion concentration

Table 2. Calculated column kinetic parameters for Pb^{2+} adsorption on NPN

Kinetic model	Flow rate			Bed height			Initial ion conc.		
	5ml/min	7.5ml/min	10ml/min	50mm	100mm	150mm	50mg/l	100mg/l	150mg/l
Thomas									
K_T(ml/min/mg)	0.05	0.075	0.1	0.05	0.05	0.05	0.1	0.075	0.067
q_0(mg/g)	37.567	38.874	41.460	75.59	39.017	25.632	6.937	37.596	41.223
R^2	0.995	0.979	0.976	0.979	0.994	0.995	0.979	0.995	0.994
Yoon & Nelson									
K_{YN} (min^{-1})	0.008	0.01	0.0011	0.008	0.008	0.008	0.007	0.008	0.010
τ (min)	1657.5	1492	1326.4	1662.5	1657.5	1503.3	1702.9	1653.8	1465
q_0 mg/g)	23.55	31.80	37.69	47.24	23.55	14.24	12.10	23.50	31.22
R^2	0.995	0.996	0.976	0.979	0.995	0.975	0.979	0.995	0.99

Table 3. Calculated column kinetic parameters for Cu^{2+} adsorption on NPN

Kinetic model	Flow rate			Bed height			Initial ion conc.		
	5ml/min	7.5ml/min	10ml/min	50mm	100mm	150mm	50mg/l	100mg/l	150mg/l
Thomas									
K_T(ml/min/mg)	0.15	0.15	0.167	0.15	0.15	0.15	0.3	0.15	0.133
q_0(mg/g)	6.008	8.981	17.224	11.922	5.789	3.759	3.417	6.497	8.957
R^2	0.985	0.983	0.982	0.989	0.988	0.974	0.986	0.989	0.977
Yoon & Nelson									
K_{YN} (min^{-1})	0.021	0.027	0.033	0.015	0.016	0.018	0.017	0.017	0.024
τ (min)	467.3	418.9	403.3	419.5	380.9	335.8	424.4	403.5	349.3
q_0(mg/g)	6.64	8.92	11.46	11.92	5.41	3.18	3.02	5.73	7.44
R^2	0.996	0.981	0.990	0.989	0.988	0.963	0.986	0.989	0.977

To evaluate the adsorption performance of an adsorbent, the mathematical model for the simulation of adsorption processes to predict the adsorption behaviour is needed (Xiang *et al.,* 2008). Yoon and Nelson model was chosen to fit the experimental data. Figs 14 and 15 present the experimental breakthrough curves obtained for each activated carbon at flow rate of 5ml/min, inlet ion concentration of 100mg/l and bed height of 100mm. The theoretical curves calculated according to the proposed model are also shown in Figs 14 and 15. It can be seen that the theoretical curve is in good agreement with those of the experimental curve. This is in agreement with the results obtained by Kavak and Öztürk (2004) and Sivakumar and Palanisamy (2009).

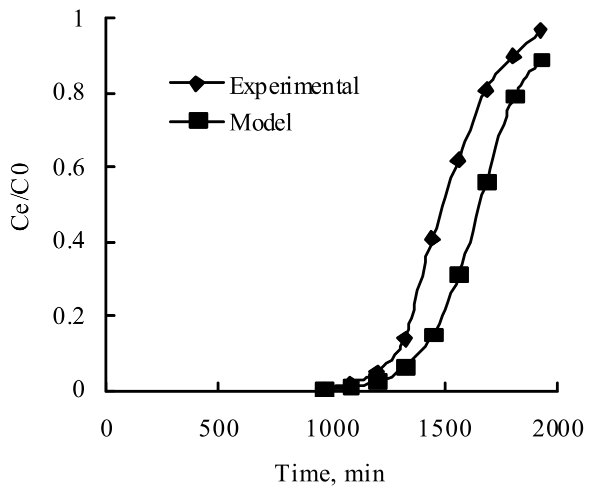

Fig. 14. Comparison of experimental and predicted curves for the adsorption of Pb^{2+} on NPN

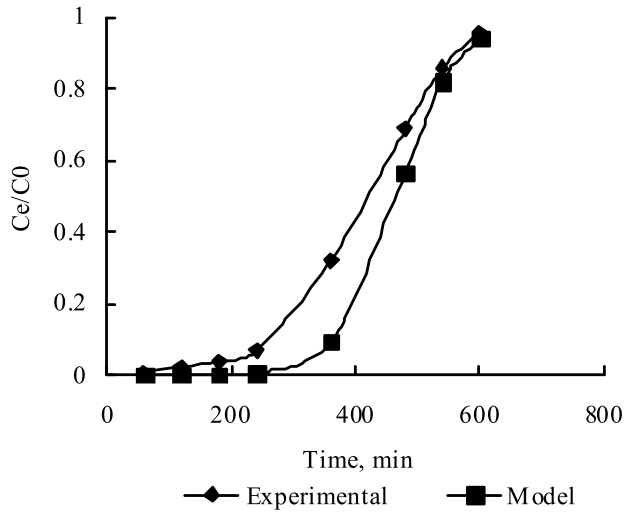

Fig. 15. Comparison of experimental and predicted curves for the adsorption of Cu^{2+} on NPN

CONCLUSION

The adsorptive removal of lead(11) and copper(11) from aqueous solution in a fixed bed column using activated carbon prepared from nipa palm nut has been investigated. Thomas and Yoon and Nelson kinetic models were used to describe the column adsorption kinetics. The experimental data fitted the kinetic models. The rate constants, adsorption capacity, and time for 50% adsorbate breakthrough were dependent on flow rate, bed height and initial ion concentration. The experimental breakthrough curve compared satisfactorily with the breakthrough profile calculated by Yoon and Nelson method. The determined column parameters can be scaled up for the design of fixed bed columns.

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