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BREAKTHROUGH CURVE STUDIES FOR THE REMOVAL OF HEAVY METALS IN A FIXED BED COLUMN

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ABSTRACT

Breakthrough curve studies for the removal of heavy metals using activated carbon derived from palmyra palm nut (PPN) was carried out in a fixed bed column. The effects of important parameters such as inlet ion concentration, flow rate and bed height on the breakthrough curve were studied. Breakthrough time increased with increase in bed height, inlet ion concentration and flow rates. Increasing the flow rate gave rise to a shorter time for saturation. Breakthrough was achieved in lesser time for Cu^{2+} adsorption than Pb^{2+} adsorption. As flow rate increased from 5 to 10ml/min breakthrough was achieved between 1200 to 1500 min for Pb^{2+} adsorption while breakthrough was reached between 220 and 350 min for adsorption of Cu^{2+}. The experimental breakthrough data correlated well with the breakthrough profile calculated by Yoon and Nelson method for activated carbon. Palmyra palm nut was found to be an efficient adsorbent for the removal of lead (11) and Copper (11) in a continuous mode using fixed bed column.

Keywords: Fixed bed column, palmyra palm nut, breakthrough curve, heavy metals, activated carbon.

INTRODUCTION

Many industries in Nigeria discharge their wastewater into surface waters (Oceans, seas, rivers and stream) without any form of remediation or treatment. Equally, the wastewaters are not properly treated before they are disposed off. An estimated 90 percent of all wastewater in developing countries is discharged untreated directly into rivers, lakes or the oceans (UNEP, 2010). These heavy metals are not biodegradable and their presence in water leads to bioaccumulation in living organisms causing health problems in animals, plants, and human beings (Ong *et al*., 2007). 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). Lead has damaging effects on body nervous system. It reduces 1.Q Level in children. 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). Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper is essential to life and health but, like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers.

Industrial effluents contain enormous quantities of inorganic and organic chemical wastes, which are steadily becoming more complex and difficult to treat by conventional technologies. Adsorption onto activated carbon has been found to be superior to other techniques 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). The major characteristic of the dynamic behaviour of fixed-bed adsorption is the history of effluent concentration (Tien, 1994). These concentration-time curves are commonly referred to as the breakthrough curves, and the time at which the effluent concentration reaches the threshold value is called the breakthrough time. The design of adsorption systems is normally based on accurate predictions of breakthrough curves for specific conditions.

Many theoretical or empirical equations have been proposed for modeling the breakthrough curves in a fixed bed adsorption. Yoon and Nelson model was used to analyze the column performance for the removal of lead (11) and copper (11) using PPN. This 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). Yoon and Nelson model is less complicated than other models and it requires no detailed data concerning the characteristics of the physical properties of the adsorption bed.

The Yoon and Nelson equation regarding to a single component system is expressed as (Kavak and Öztürk, 2004).

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$$\frac{C_e}{C_o} = \frac{1}{1+\exp[K(\tau - t)]} \qquad (1)$$

Where k is the rate constant (l/min), τ the time required for 50% adsorbate breakthrough (min) and t is the breakthrough (sampling) time (min). The linearized form of the Yoon and Nelson model is as follows:

$$In\,\frac{C_e}{C_o - C_e} = k\,t - \tau k \qquad (2)$$

This is aimed at applying a simple model proposed by Yoon and Nelson for modeling the breakthrough curves of lead (11) and Copper (11) in a fixed bed packed with activated carbon. The effects of parameters such as initial ion concentration, flow rate and bed height on the breakthrough curves were investigated.

MATERIALS AND METHODS

Preparation of activated carbon

Palmyra palm nuts were obtained from the premises of Nnamdi Azikiwe University, Awka, Nigeria. The palm nuts were thoroughly 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 2:2 (on weight basis). The impregnated sample was dried in an oven at 120^{o}C for 24hrs. The dried sample was carbonized in a Muffle furnace for 2hours 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.

Characterization of activated carbon

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; 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.

Breakthrough studies

Experimental procedure

Breakthrough studies were carried out using a glass column of 30mm internal diameter and 300mm length. The 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 as shown in figure 1. Three different bed heights

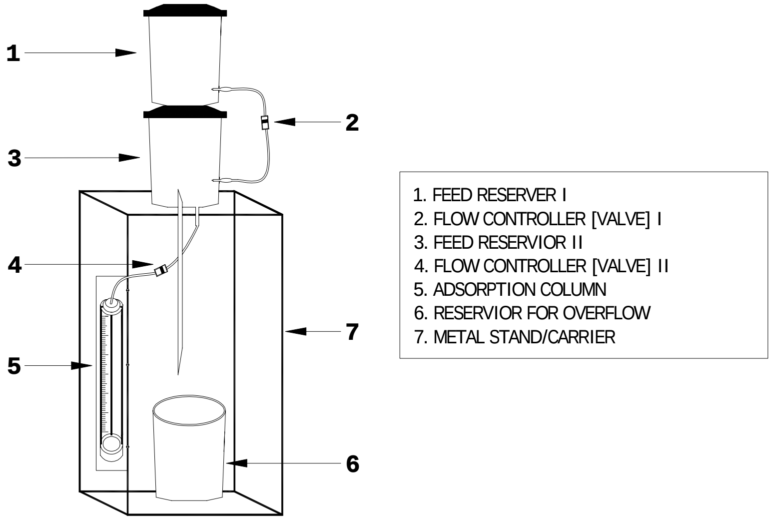

Fig.1. Schematic diagram of the mini adsorption column.

(50mm, 100mm and 150mm) were used. The tank containing the heavy metal solution was placed at a higher elevation so that the metal solution could be 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 avoid fluctuation of the flow rate of the solution being delivered to the column. The second flow controller helps to regulate the flow rate. Three flow rates (5, 7.5 and 10ml/min) and three inlet ion concentrations of 50, 100 and 150mg/l were used. The effluent samples were collected at specified intervals and analyzed for the residual Pb^{2+} and Cu^{2+} concentrations using atomic adsorption spectrophotometer at 217nm and 324.8nm respectively. Column studies were terminated when the column reached exhaustion.

RESULTS AND DISCUSSION

Characteristics of activated carbon derived from nipa palm nut

Table 1. Physico-chemical characteristics of activated carbon derived from palmyra palm nut.

Properties	**Values**
pH	6.8
Bulk density, g/cm^3	0.61
Iodine number, mg/g	785.78
Moisture content, %	4.10
Volatile matter, %	18.14
Ash content, %	3.40
Fixed carbon, %	78.56
Surface Area, m^2/g	820.37

Breakthrough Studies

Calculation of breakthrough curve is helpful in the design of packed bed (Reinik *et al*., 2001; Kavak and Öztürk, 2004).

Effect of flow rate on breakthrough curves

The effect of flow rate for the adsorption of Pb^{2+} and Cu^{2+}onto activated carbon derived from palmyra palm nut was studied at flow rates of 5, 7.5 and 10ml/min, inlet ion concentration of 100mg/l and bed height of 100mm as shown in Figures 2 and 3. From figures 2 and 3, it is seen that rapid uptake of metal ion is noticed in the initial stages and rate decreased thereafter and finally reached saturation. This is in agreement with the result obtained by Sivakumar and Palamisamy (2009). When the volumetric flow rate decreased from 10 to 5ml/min more favourable ion exchange conditions were achieved (Kananpanah *et al*., 2009). As flow rate increased, the breakthrough curves become steeper and reached the breakthrough quickly. This is because of the residence time of the adsorbate in the column, which is long enough for adsorption equilibrium to be reached at high flow rate. This means that the contact time between the adsorbate and the adsorbent is minimized, leading to early breakthrough (Sivakumar and Palanissamy, 2009). Increasing the flow rate gave rise to a shorter time for saturation. Breakthrough was achieved between 1200 to 1500 min for Pb^{2+} adsorption while breakthrough was reached between 220 and 350 min for adsorption of Cu^{2+}. This implies that PPN is a better adsorbent for the adsorption of $Pb^{2+.}$

Effect of bed height on breakthrough curves

Breakthrough curves for the adsorption of Pb^{2+} and Cu^{2+} onto PPN at various bed heights, at the inlet concentration of 100mg/l and flow rate of 5ml/min are shown in figures 4 and 5. The results indicate that the throughput volume of the aqueous solution increased with increase in bed height, due to the availability of more number of sorption sites (Sivakumar and Palanisamy, 2009). The equilibrium sorption capacity decreased with increase in bed height. This shows that at smaller bed height the effluent adsorbate concentration ratio increased more rapidly than for a higher bed height. Furthermore, the bed is saturated in less time for smaller bed heights. Small bed height corresponds to less amount of adsorbent.

3.2.2. Effect of initial ion concentration on breakthrough curves

The effect of inlet ion concentration on the breakthrough curves at bed height of 100mm and flow rate of 5ml/min is shown in Figure 6 and 7. It is observed that as the initial ion concentration increased from 50 to 150mg/l, the break point time decreased. On increasing the initial ion concentration, the breakthrough curves became steeper and breakthrough volume decreased because of the lower mass-transfer flux from the bulk solution to the particle surface due to the weaker driving force (Sivakumar and Palanisamy, 2009; Baek *et al*., 2007). At higher concentration the availability of the metal molecules for the adsorption sites is more, which leads to higher uptake of Pb^{2+} at higher concentration even though the breakthrough time is shorter than the breakthrough time of lower concentrations.

Modelling the behaviour of Pb^{2+} and Cu^{2+} in a fixed bed adsorption column

Evaluation of the adsorption performance of an adsorbent requires the mathematical model for the simulation of adsorption processes in order to predict the adsorption behaviour (Xiang *et al*., 2008). Yoon and Nelson model was chosen to fit the experimental data. The experimental breakthrough curves obtained at flow rate of 5ml/min, inlet ion concentration of 100mg/l and bed height of 100mm are presented in figures 8 and 9. The theoretical curves calculated from the proposed model are also shown in figures 8 and 9. It can be seen that the

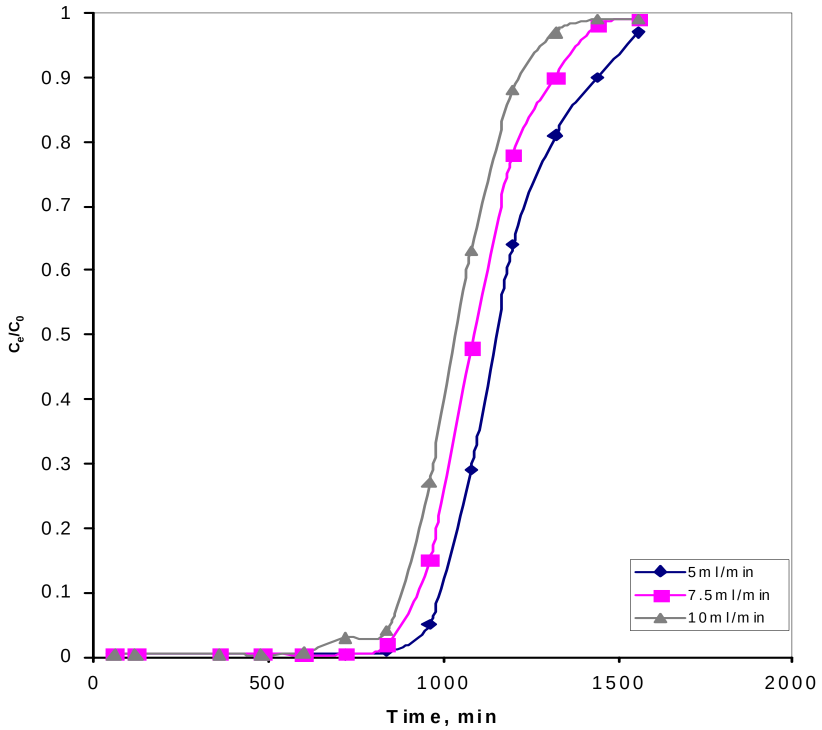

Fig. 2. Effect of flow rate on breakthrough curve for Pb^{2+} adsorption on PPN.

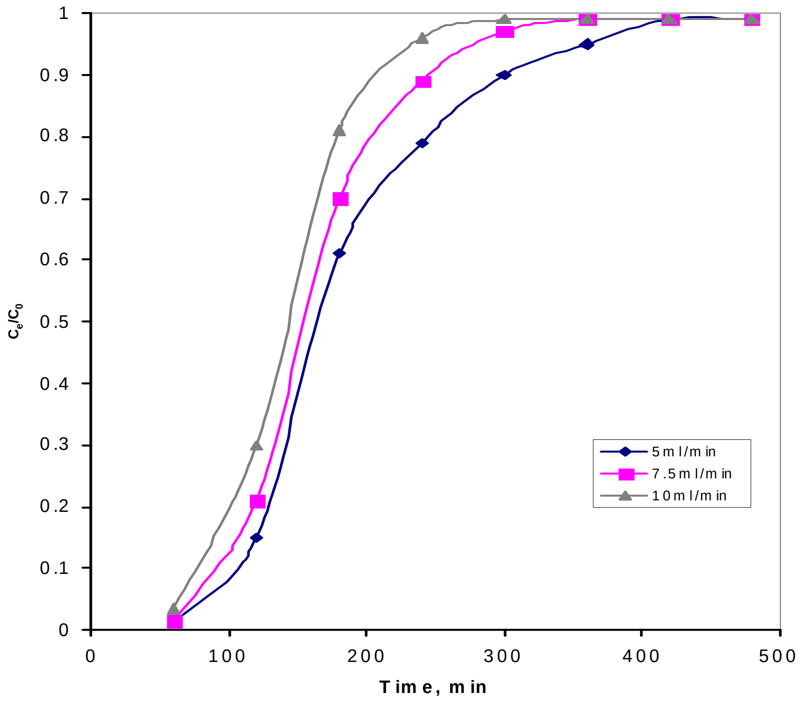

Fig. 3. Effect of flow rate on breakthrough curve for Cu^{2+} adsorption on PPN.

theoretical curves are in good agreement with those of the experimental ones. This means that the slopes of the breakthrough curves that were produced approximate closely to the experimental breakthrough curves. This is in agreement with the results obtained by Kavak and Öztürk (2004) and Sivakumar and Palanisamy (2009).

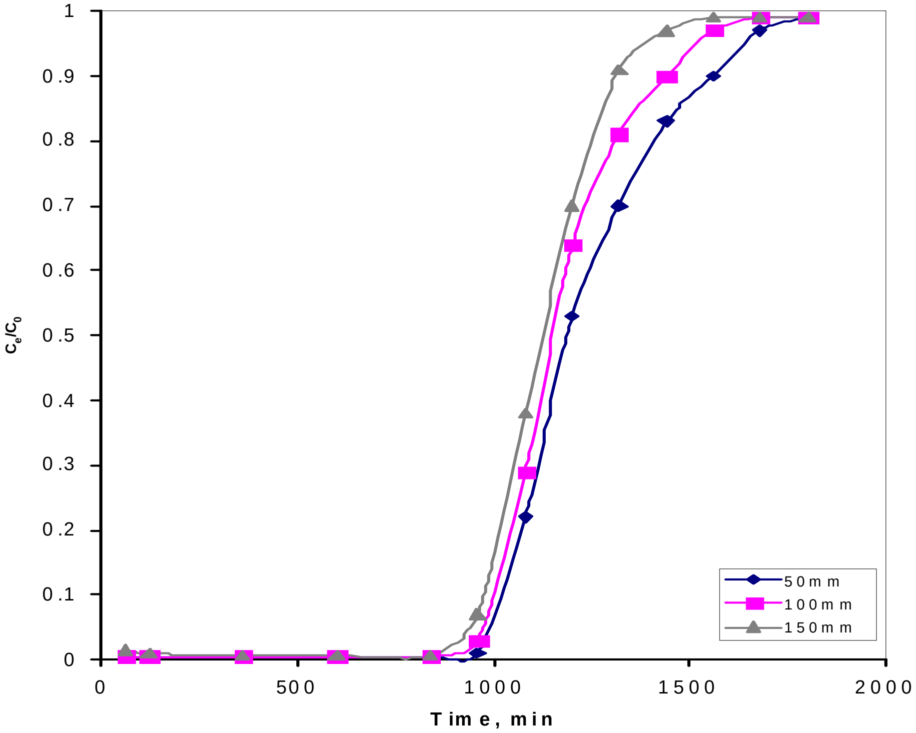

Fig. 4. Effect of bed height on breakthrough curve for Pb^{2+} adsorption on PPN.

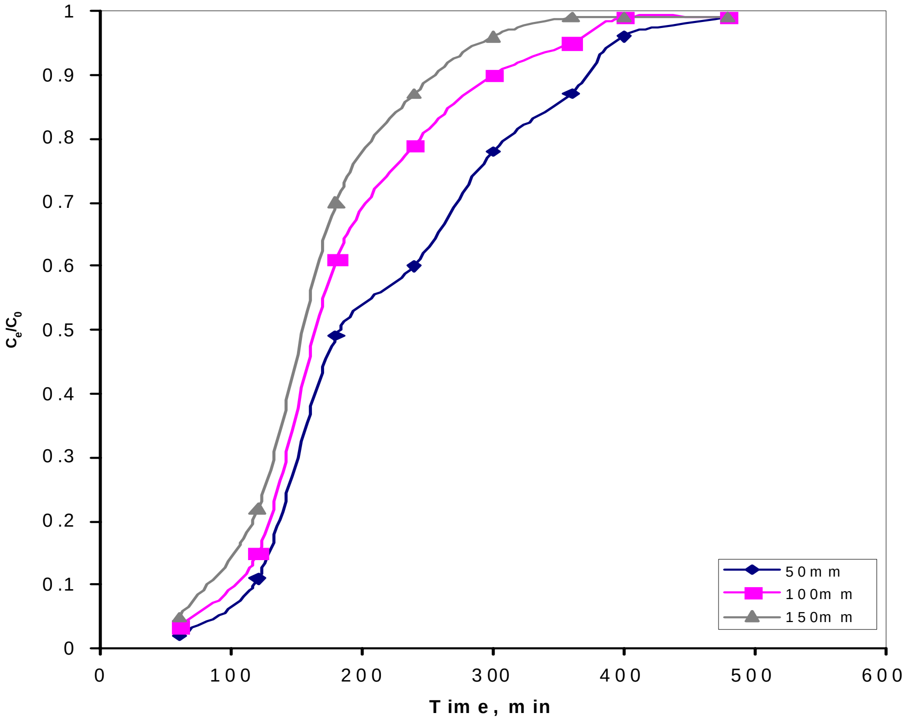

Fig. 5. Effect of bed height on breakthrough curve for Cu^{2+} adsorption on PPN.

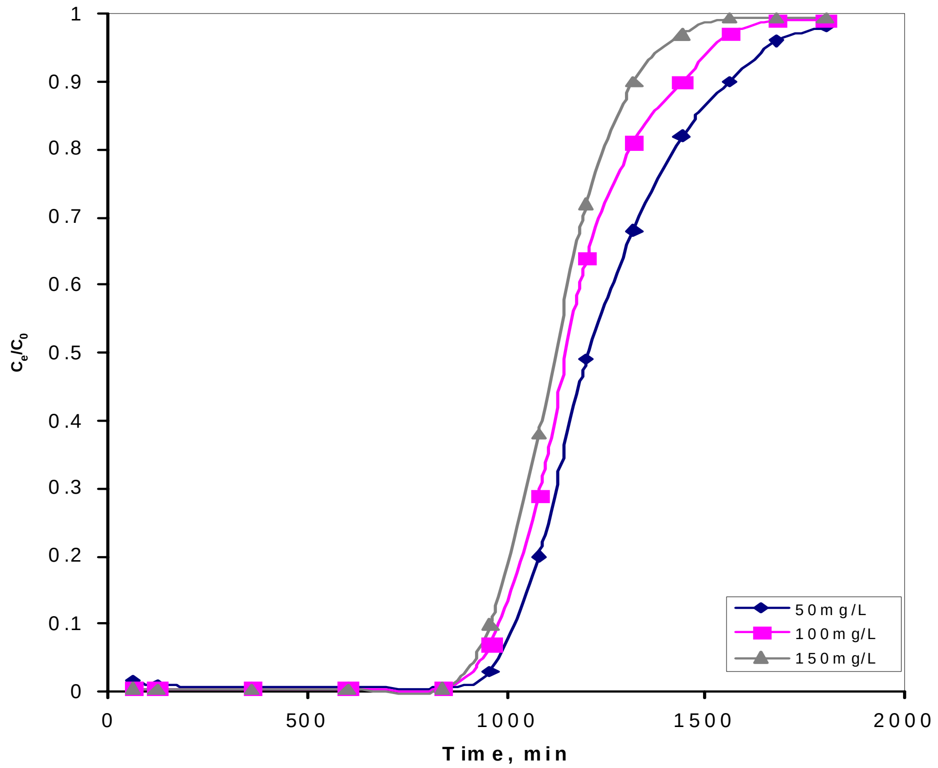

Fig. 6. Effect of initial ion concentration on breakthrough curve for Pb^{2+} adsorption on PPN.

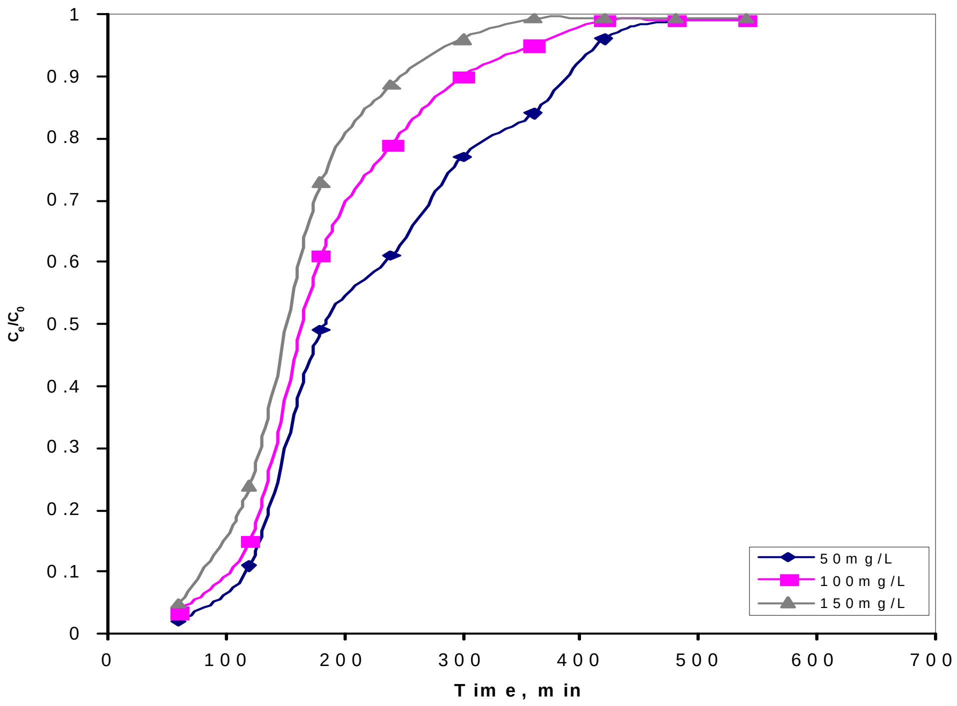

Fig.7. Effect of initial ion concentration on breakthrough curve for Cu^{2+} adsorption on PPN.

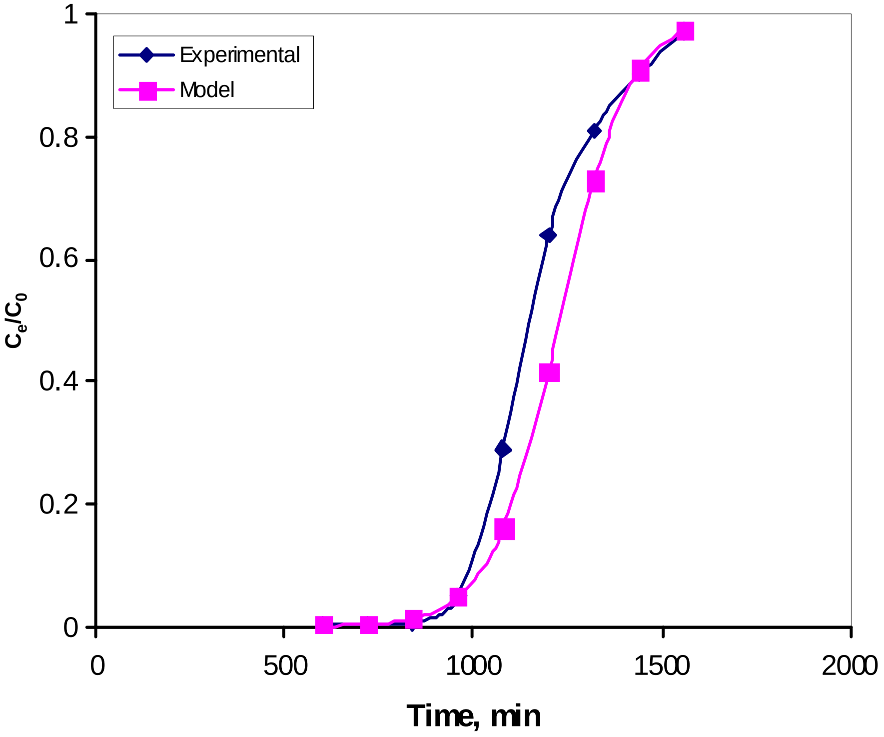

Fig. 8. Comparison of experimental and predicted curves for the adsorption of Pb^{2+} on PPN.

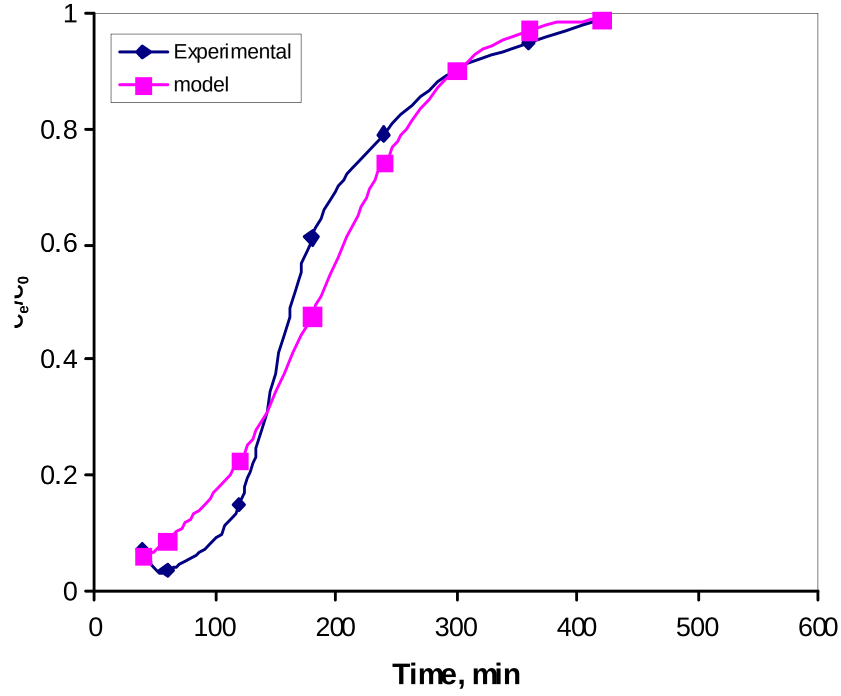

Fig. 9. Comparison of experimental and predicted curves for the adsorption of Cu^{2+} on PPN.

CONCLUSION

Breakthrough studies for the adsorption of Pb^{2+} and Cu^{2+} onto the activated carbon derived from palmyra palm nut at different flow rates of 5, 7.5 and 10ml/min, an inlet ion concentration of 100mg/l and bed height of 100mm in a fixed bed column has been carried out. The effects of inlet ion concentration, flow rate and bed height on the breakthrough curves showed that breakthrough time increased with increase in the inlet ion concentration and bed height and decreased with increasing flow rate. The calculated theoretical breakthrough curves from Yoon and Nelson model was in agreement with the experimental breakthrough profiles.

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