# Adsorption Performance of Packed Bed Column for the removal of Lead (ii) using oil Palm Fibre

**Nwabanne, J. T.**

**Igbokwe, P. K.**

Department of Chemical Engineering
Nnamdi Azikiwe University
P.M.B. 5025, Awka
Nigeria

## Abstract

*The adsorption performance of packed bed column using activated carbon prepared from oil palm fibre (OPF) for the removal of lead (11) from aqueous solution was investigated. The influence of important parameters like inlet ion concentration, flow rate and bed height on the breakthrough curves and adsorption performance was studied. The result indicated that adsorption efficiency increased with increase in the inlet ion concentration and bed height and decreased with increase in flow rate. Increasing the flow rate resulted to a shorter time for saturation. The result revealed that the throughput volume of the aqueous solution increased with increase in bed height, due to the availability of more number of sorption sites. The adsorption kinetics was analyzed using Thomas and Yoon and Nelson kinetic models. The kinetic data were well described by both models. The maximum adsorption capacity, calculated from both models, 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 correlated well with both models. The comparison of the experimental breakthrough curve to the breakthrough profile obtained from Yoon and Nelson method showed a satisfactory fit for activated carbon derived from oil palm empty fruit bunch.*

**Keywords:** Packed bed column, oil palm fibre, lead, removal, adsorption

## *1. Introduction*

Water pollution remains a major problem in the Nigerian environment. Both urbanization and industrialization have contributed to the large scale of pollution. Most of the time wastewater is discharged into the streams, wells, rivers and other water bodies without treatment or improper treatment. Pollution from wastewater depreciates land values, increases municipal costs and causes numerous adverse biological and human health effects. 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.

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). Activated carbons are usually obtained from materials with high carbon content and possess a great adsorption capacity, which is mainly determined by their porous structure (Otero et al, 2003). The inherent nature of the precursor or starting material, as well as the method and conditions employed for carbon synthesis, strongly affects the final pore size distribution and the adsorption properties of the activated carbons (Shopova et al, 1997, Biota et al, 1997).Oil palm fibre (OPF), or mesocarpfibre, is the fibre obtained after expressing oil from the fruit mesocarp. For every tonne of fresh fruit bunches (FFB) processed, 120kg of OPF is produced (Aziz et al, 2002).

OPF contains on a dry weight basis, approximately 40% cellulose, 21% lignin, 24% pentosan and 5% ash (Kirkaldy and Sutanto, 1976). Nigeria is a major producer of palm oil with oil palm fibre as a waste biomass.
The major characteristic of fixed-bed adsorption is the history of effluent concentration (Tien, 1994). These concentration-time curves (or their equivalents) 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 rational design of adsorption systems is based on accurate predictions of breakthrough curves for specific conditions. Despite the usefulness of fixed-bed mode, its analysis is usually complex. Fixed-bed operation is influenced by equilibrium (isotherm and capacity), kinetic (diffusion and convention coefficients), and hydraulic (liquid hold-up, geometric analysis, and mal-distribution) factors (Inglezakis and Poulopoulos, 2006). Two models (Thomas model and Yoon and Nelson model) were used to analyze the column performance for the removal of lead (11) from aqueous solution using OPF.

**Thomas – BDST Model**

The Thomas model is known as the bed-depth-service-time (BDST) model (Kavak and Öztűrk, 2004). The BDST approach is based on the irreversible isotherm model by Bohart and Adams (Inglezakis and Poulopoulos, 2006). This simplified-design model ignores both the intraparticle (solid) mass transfer resistance and the external (fluid-film) resistance directly. This means that the rate of adsorption is controlled by the surface reaction between the adsorbate and the unused capacity of the adsorbent. This expression by Thomas for an adsorption column is given as follows (Baek et al, 2007)

$$\frac{C_e}{C_o} = \frac{1}{1+\exp\left[\frac{K_T}{Q}\left(q\ M - C_o V\right)\right]} \qquad (1)$$

The linearized form of the Thomas model is as equation (2) (Kavak and Öztürk, 2004):

$$In\left(\frac{C_o}{C_e} - 1\right) = \frac{K_T q_o M}{Q} - \frac{K_T C_o}{Q} V \qquad (2)$$

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).

**Yoon and Nelson model**

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). The Yoon and Nelson equation regarding to a single component system is expressed as (Aksu and Gönen, 2004):

$$\frac{C_e}{C_o} = \frac{1}{1+\exp\left[K\left(\tau - t\right)\right]} \qquad (3)$$

Where kis the rate constant (l/min), $\tau$ is 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:

$$In\ \frac{C_e}{C_o - C_e} = k\,t - \tau k \qquad (4)$$

## *2. Experimental*

### 2.1 Preparation of activated carbon

Oil palm fibre was obtained from Ichida women co-operative oil processing mill, Ichida, Anambra State, Nigeria.

The raw material was washed several times using de-ionized water to remove all traces of impurities, oil, dirt, dust, etc. The material was dried in the sun for 72 hours to remove excess water until constant weight was obtained. The bunch was 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 (on weight basis). The impregnated sample was dried in a Memmert oven at $120^0$C for 24hrs. The dried sample was carbonized in a Muffle furnace for 2hr at $800^0$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.

### 2.2 Characterization of activated carbon

The pH of the activated 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.

### 2.3 Column studies

#### 2.3.1 Experimental procedure

Fixed bed column 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 . Bed height of 50mm, 100mm and 150mm was 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) were used while initial ion concentrations of 50, 100 and 150mg/l were used. The effluent samples were collected at specified intervals and analyzed for the residual $Pb^{2+}$ concentration using atomic adsorption spectrophotometer at 217nm. Column studies were terminated when the column reached exhaustion. The schematic diagram is shown in Figure 1.

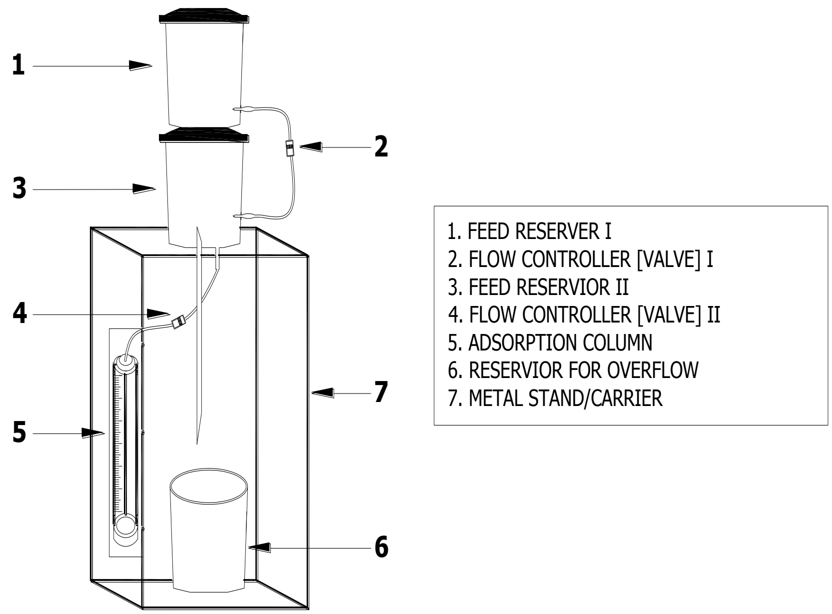


**Fig.1: Schematic diagram of packed bed column**

## *3. Results and Discussion*

Physico-chemical characteristics of activated carbon derived from oil palm fibre are shown in Table 1.
Table 1: Physico-chemical characteristics of activated carbon derived from oil palm fibre

| Properties | Values |
|---|---|
| pH | 6.6 |
| Bulk density, $g/cm^3$ | 0.56 |
| Iodine number, mg/g | 676.88 |
| Moisture content, % | 3.43 |
| Volatile matter, % | 23.61 |
| Ash content, % | 4.39 |
| Fixed carbon, % | 72.0 |
| Surface Area, $m^2/g$ | 715.63 |

### 3.1 Column Studies

### 3.1.1 Breakthrough curves

The design of packed bed adsorber involves mainly the calculation of breakthrough curves (Reinik et al, 2001; Kavak and Öztürk, 2004)

**Effect of flow rate on breakthrough curves**

The effect of flow rate for the adsorption of $Pb^{2+}$ onto the empty fruit bunch at flow rates of 5, 7.5 and 10ml/min, at an inlet ion concentration of 100mg/l and bed height of 100mm is shown in Figure 2. From Figure 2, 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.

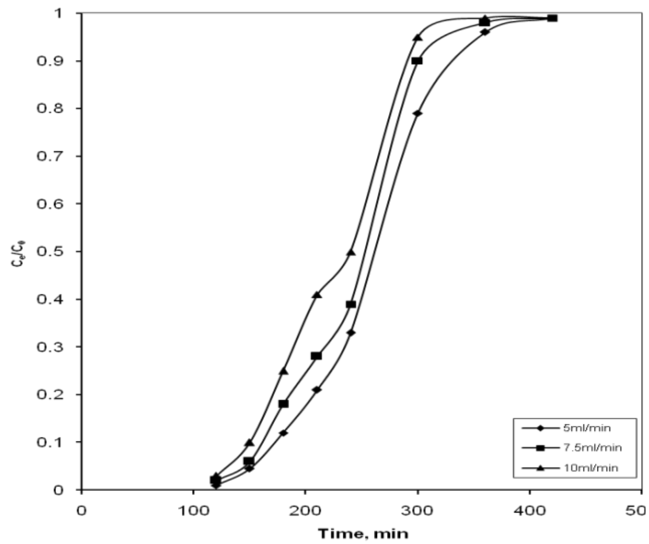


**Fig. 2: Effect of flow rate on breakthrough curve for $Pb^{2+}$ adsorption on OPF**

**Effect of bed height on breakthrough curves**

Breakthrough curves for the adsorption of $Pb^{2+}$ onto EFB at various bed heights, at the inlet concentration of 100mg/l and flow rate of 5ml/min are shown in Figure 3. 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. Further more, the bed is saturated in less time for smaller bed heights. Small bed height corresponds to less amount of adsorbent.

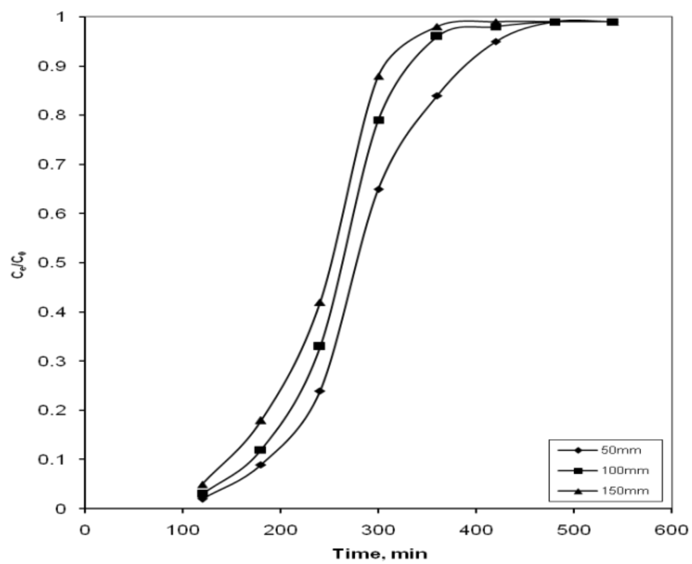


**Fig. 3: Effect of bed height on breakthrough curve for $Pb^{2+}$ adsorption on OPF**

**Effect of initial ion concentration on breakthrough curves**

The effect of inlet adsorbate concentration on the breakthrough curves at bed height of 100mm and flow rate of 5ml/min is shown in Figure 4. 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.

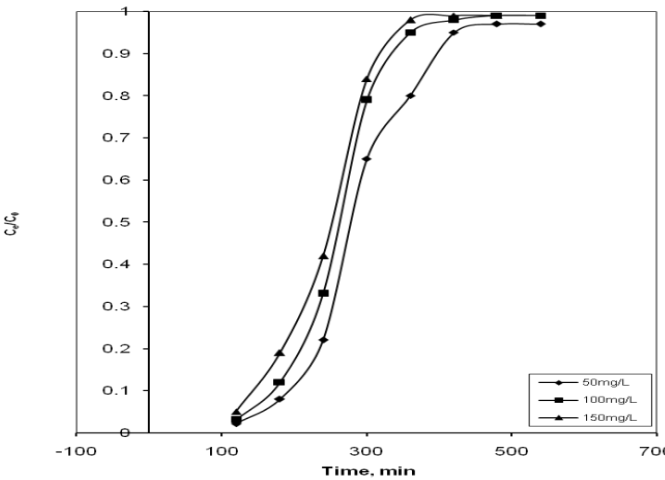


**Fig. 4: Effect of initial ion concentration on breakthrough curve for $Pb^{2+}$ adsorption on OPF**

### 3.1.2 Column kinetic study

Two models (Thomas model and Yoon and Nelson model) were used to analyze the column performance.

**Thomas model**

Thomas model has been used by many researchers to study packed bed adsorption kinetics (Kavak and Öztürk, 2004.,Baek et al, 2007., Sivakumar and Palanisamy, 2009).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 (Figures 5, 6 and 7). The results of $K_T$, $R^2$ and $q_o$ are given in Table 2. Thomas rate constant,$K_T$ is dependent on flow rate, initial ion concentration and 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. 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).

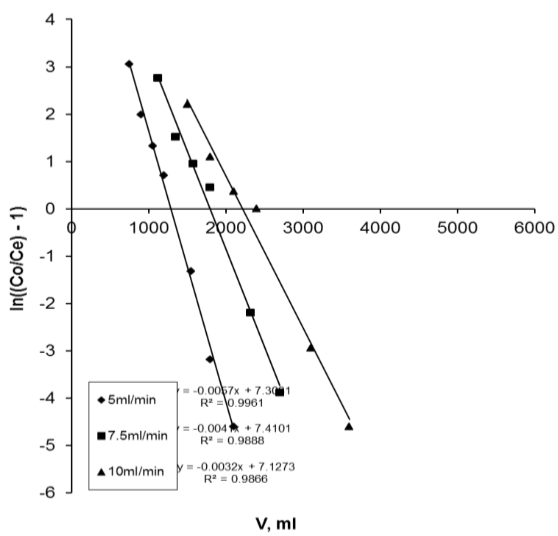


**Fig. 5: Thomas kinetic plot for the adsorption of $Pb^{2+}$ on OPF: Effect of flow rate**

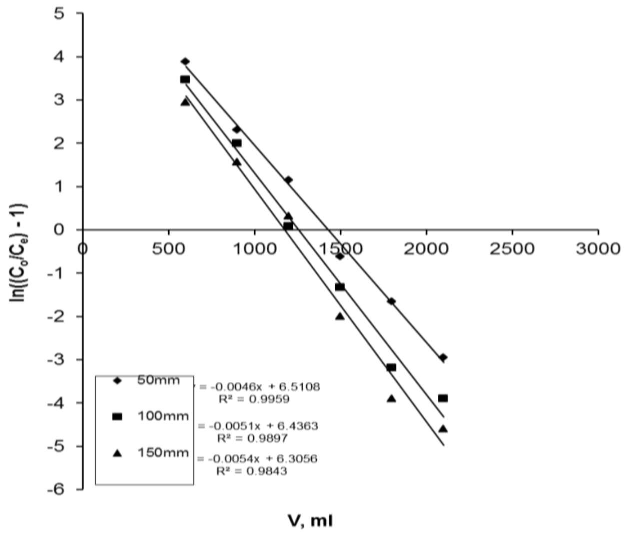


**Fig. 6: Thomas kinetic plot for the adsorption of $Pb^{2+}$ on OPF: Effect of bed height**

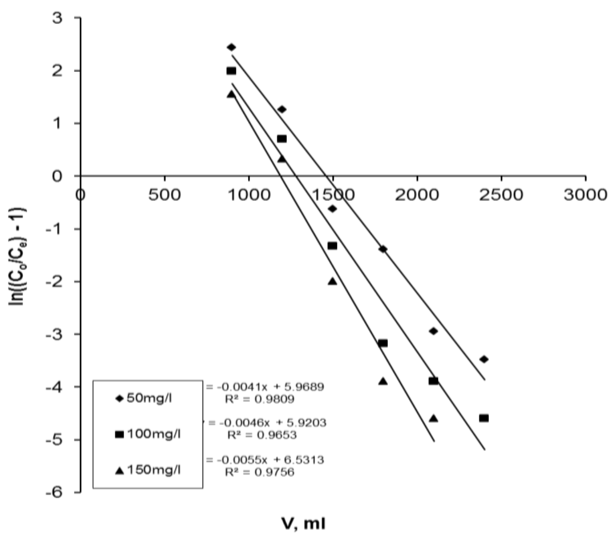


**Fig. 7: Thomas kinetic plot for the adsorption of $Pb^{2+}$ on OPF: Effect of initial ion concentration**

**Yoon and Nelson model**

Several authors have used Yoon and Nelson model in the study of column adsorption kinetics (Tsai et al, 1999., Kavak and Öztürk, 2004., Sivakumar and Palanisamy, 2009). A plot of In $C_e/(C_o-C_e)$ versus t gives a straight line with slope of $K_{YN}$, and intercept of $-\tau.K_{YN}$(Figures 8, 9, 10). The values of $K_{YN}$, τ and adsorption capacity, $q_o$ obtained are listed in Table 2. The results show that therate constant, $K_{YN}$ increased with increased inlet ion concentration, flow rate and bed height. 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 time required for 50% breakthrough, τ decreased with increase in flow rate, flow rate and 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).

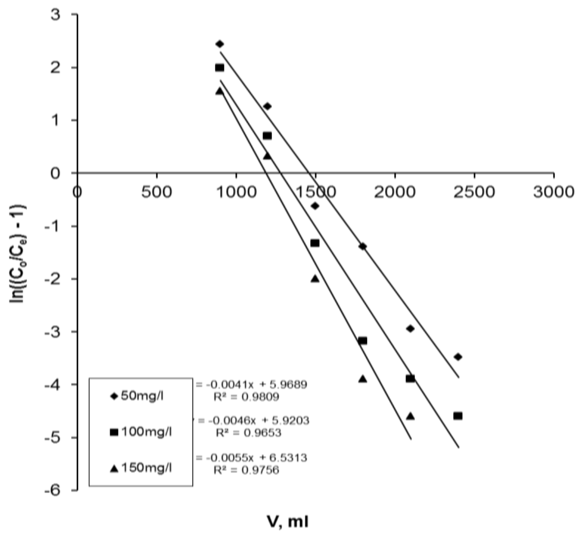


**Fig. 8: Yoon and Nelson kinetic plot for the adsorption of $Pb^{2+}$ on OPF: Effect of flow rate**

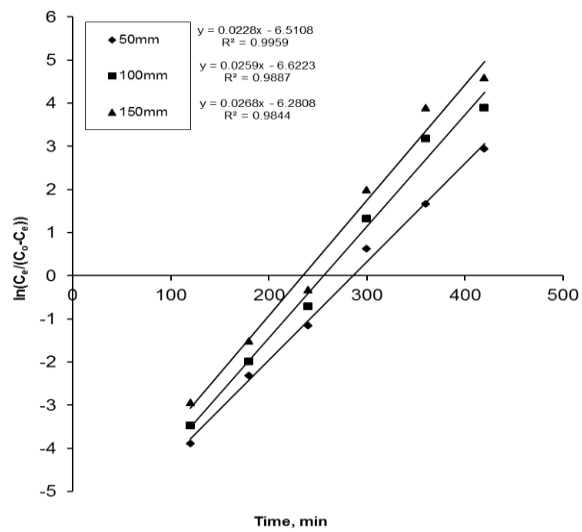


**Fig. 9: Yoon and Nelson kinetic plot for the adsorption of $Pb^{2+}$ on OPF: Effect of bed height**

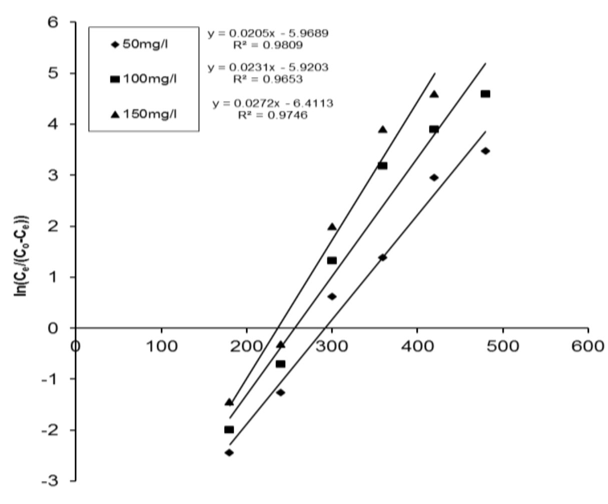


**Fig. 10: Yoon and Nelson kinetic plot for the adsorption of $Pb^{2+}$ on OPF: Effect of initial ion concentration**

**Table 2: Calculated column kinetic parameters for $Pb^{2+}$ adsorption on OPF.**

| Kinetic model | Flow rates | | | 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) | 0.25 | 0.3 | 0.3 | 0.2 | 0.25 | 0.25 | 0.4 | 0.2 | 0.167 |
| $q_0$(mg/g) | 3.928 | 4.983 | 6.390 | 8.754 | 3.462 | 2.261 | 2.006 | 3.981 | 5.259 |
| $R^2$ | 0.996 | 0.988 | 0.986 | 0.995 | 0.989 | 0.984 | 0.980 | 0.965 | 0.975 |
| **Yoon & Nelson** | | | | | | | | | |
| $K_{YN}$ ($min^{-1}$) | 0.028 | 0.028 | 0.032 | 0.022 | 0.025 | 0.026 | 0.020 | 0.023 | 0.027 |
| τ(min) | 260.8 | 245.1 | 222.7 | 295.9 | 264.9 | 241.5 | 298.4 | 257.4 | 237.4 |
| $q_0$(mg/g) | 3.51 | 4.94 | 5.99 | 7.96 | 3.56 | 2.167 | 2.01 | 3.46 | 4.79 |
| $R^2$ | 0.996 | 0.983 | 0.986 | 0.995 | 0.988 | 0.984 | 0.980 | 0.965 | 0.974 |

### 3.1.3 Modelling the behaviour of $Pb^{2+}$ in a fixed bed adsorption column

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. Figure 11 presents 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 Figure 11. 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).

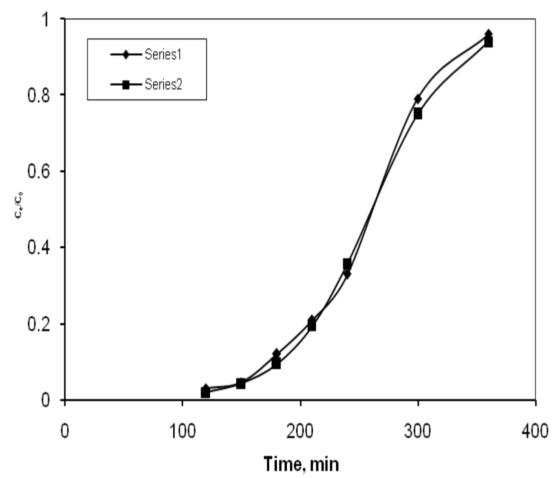


**Figure 11: Comparison of experimental and predicted curves for the adsorption of $Pb^{2+}$ on OPF**

### 5. References

Ahmad, A.A., Hameed, B.H. & Aziz, N. (2006). Adsorption of direct dye on palm ash: kinetic and equilibrium modeling. Journal of Hazardous Materials, 094, 1-10.

Ahmedna, M., Johns, M.M., Clarke, S.J., Marshall, W. E. & Rao, R. M. (1997).Potential of agricultural by-product-based activated carbons for use in raw sugar decolourisation. Journal of the Science of Food and Agriculture, 75, 117-124.

Aksu, Z., & Tezer, S. (2000). Equilibrium and kinetic modelling of bisorption of remazol black B by Rhizopusarrhizus in a batch system: effect of temperature. Process Biochemistry, 36, 431-439.

Al-Qodah, Z., & Shawabkah, R. (2009). Production and characterization of granular activated carbon from activated sludge. Braz. J. Chem. Eng., 26(1), 6.

Alzaydian, A. S. (2009). Adsorption of methylene blue from aqueous solution onto a low – cost natural Jordanian Tripoli. Am. J. Applied Sci., 6(6), 1047-1058.

American Society for Testing and Materials. (1996). Annual Book of ASTM Standard, Volume 15.01, Refractories, Carbon and Graphic Products; activated Carbon, ASTM, Philadelphia, PA.

American Society for Testing and Materials. (1986). Standard test method for determination of iodine number of activated carbon. Philadelphia, PA: ASTM Committee on Standards.

American Society of Testing and Materials. (1991). Standard test methods for moisture in activated carbon. Philadelphia, PA: ASTM Committee on Standards.

Aziz, A. A., Das, K., Husin, M., & Mokhtar, A. (2002). Effects of physical and chemical Pre-treatments on xylose and glucose production from oil palm press fibre, Journal of Oil Palm Research, 14(2), 10-17.

Baek, K., Song, S., Kang, S., Rhee, Y., Lee, C., Lee, B., Hudson, S., & Hwang, T. (2007). Adsorption kinetics of boron by anion exchange resin in packed column bed. J. Ind. Eng. Chem., 13(3), 452-456.

Bóta, A., László, K., Nagy, L.G., & Copitzky, T. (1997). Comparative study of active carbons from different precursors.Langmuir, 13, 6502.

Inglezakis, V. J., & Poulopoulos, S. G. (2006). Adsorption, ion exchange and Catalysis: Design of Operation and Environmental Applications, 1stedn, Elsevier Publishers, Amsterdam, 16-17.

Kananpanah, S., Ayazi, M., & Abolghasemi, H. (2009). Breakthrough curve studies of purolite A-400 in an adsorption column. Petroleum and Coal, 51(3), 189-192.

Kavak, D., & Öztürk, N., (2004). Adsorption of boron from aqueous solution by sepirolite: II. Column studies. II. Illuslrararasi. Bor. Sempozyumu, 23-25, 495-500.

Ong, S., Seng, C., & Lim, P. (2007). Kinetics of adsorption of Cu (II) and Cd (II) from aqueous solution on husk and modified rice husk. EJEAFche, 6 (2), 1764-1774.

Qaiser, S., Saleem, A. R., & Ahmed, M. M. (2007). Heavy metal uptake by agro based waste materials. Environmental Biotechnol., 10(3), 1-8.

Otero, M., Rozada, F., Garcoia, A., & Moran, A. (2003). Kinetic and equilibrium modeling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges. Biochemical Engineering Journal, 15, 59-68.

Reinik, J., Viiroja, A., & kallas, J. (2001). Xylidine – polluted groundwater purification: adsorption experiments and breakthrough calculations. Proc. Estonian Acad. Sci. Chem., 50(4), 205-216.

Shopova, N., Minkova, V., & Markova, K. (1997). Evaluation of the thermochemical changes in agricultural by-products and in the carbon adsorbents obtained from them. J, Thermal Anal., 48, 309.

Sivakumar, P., & Palanisamy, P. N. (2009). Adsorption studies of basic Red 29 by a non-conventional activated carbon prepared from Euphorbia antiquorum L. International Journal of Chem. Tec. Research, 1 (3), 502-510.

Tien, C. (1994). Adsorption Calculations and Modelling 1st edition, Butterworth-Heinemann Publishers, USA, 1-8.

Tsai, W. T; Chang, C. Y; Ho, C. Y; & Chen, L. Y. (1999). Simplified description of adsorption breakthrough curves of 1,1-sdichloro-1-fluoroethane (HCFC – 141b) on activated carbon with temperature effect. Journal of Colloid and Interface Science. 214, 455-458.