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THE CONTINOUS STUDY OF ADSORPTION OF Pb (II) ON MODIFIED MAIZE HUSK IN A LABORATORY COLUMN

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ABSTRACT

In this study, adsorption of Pb (II) on modified maize husk was carried out on a laboratory scale column of internal diameter 2.76 cm and length of 30 cm. the effect of bed depth, flow rate, and initial metal ion concentration was varied for optimum column efficiency. The characterisation of the maize husk was carried out using SEM and FT-IR. From the result; SEM indicated appreciable pores before sorption and parked pores after sorption while functional groups like the amides, carboxyls and hydroxyls helped in the adsorption process. The column efficiency revealed at flow rate of (1, 1.5 and 2.5 ml/min), bed depth of (4, 8 and 12 cm), and initial metal concentration of (6, 10 and 20 mg/L), 94.9% of Pb (II) was removed with adsorption capacity of 10.74 mg/L achieved. Adsorption isotherms showed that the Adams-Bohartmodel described the kinetics of the process and revealed good correlation with the experimental work.

Keywords: *adsorption, Pb (II), maize husk and column*

INTRODUCTION

Industrial wastes are materials that are by products of human activities such as liquid industrial discharge or sewage (GISO 14001, 2000). It has been discovered that Nature can cope with small amount of pollutants, but it will have high negative impact or almost becomes uncontrollable if the unquantifiable amount of waste water and sewages released into the environment continuously are not remedied before discharge (Hays, 2009). Recently, heavy metal ions has become a significant pollutant which has detrimental effect on the ecosystem due to the increasing number of production and processing companies (fuel producing, energy, fertilizer, mining, leather, pesticide, metal surface treating, and aerospace etc.) (Jarupt, 2003).

When effluent containing heavy metals are knowingly or unknowingly discharged into the environment, it may lead to a serious environmental pollution and even become

highly detrimental to human life (Sudaryanto *et al.*, 2006). The living organisms that are exposed to excessive amount of this heavy metal are greatly affected; effects ranging from damage of central nervous system to corrosion of living tissue (Alemayehu, 2004). Some of the highly toxic heavy metals that may cause harmful effects when they come in contact with human include: cadmium ions (Cd^{2+}), this is known to cause tubular and glomerular damage, proteinuria, anemia, kidney damage (Cossich, 2002) ; Lead (Pb^{2+}) is known as a causative agent for kidney damage, and lead encephalopathy (Cossich, 2002) ; Copper ions (Cu^{2+}) known to cause severe mucosal irritation (Jarup, 2003) etc. Though several treatment methods have been considered for the treatment of waste water, these include: precipitation, coagulation reverse osmosis, electro dialysis and flotation to mention a few (Yahya, 2014). Most of the methods suffer some setback like generation of secondary pollutants,

expensiveness of the process and low efficiency for low heavy metal concentrations (Hays, 2009).Different biomass have been studied for heavy metal pollution remediation in different parts of the world which include maize peel (Jude, 2007), maize tassels (Okonkwo et al., 2012), bacterial (Lu et al., 2006), anaerobically digested sludge (Jarup, 2003), algae (Sudaryanto et al., 2006), fungi (Guo et al., 2005), etc.

Adsorption is a greatly preferred method for the remediation of heavy metal ions in waste water treatment, generally due to its high efficiency, simplicity in handling, high availability of the raw materials as well as its cost effectiveness (Hays, 2009). Besides, adsorption technology also has the ability for regeneration and recovery of some of the useful waste materials from the waste water. This can help to reduce cost and as such, the demand for adsorbents are increasing as more industries are required to treat their waste water under a stricter condition as regulated by law (Philomina and Enoch, 2012).

The biomass has unique structural properties which are the presence of amino, sulphate, the oether, hydroxyl, nitro, sulphydryl, carboxyl, phosphate, phenol, amides groups etc. in their functional groups hence producing a binding surface for heavy metals adsorption (Kaewsarn et al., 2008). These present study reveals the use of maize peel for the remediation of Pb (II) ion in an aqueous solution. Maize (Zea mays) peel otherwise known as maize husk was preferred in this study because of its relative abundance in Nigeria and it is a major annual crop in Nigeria hence, large volume of waste (Abia, 2007) is produced. Maize is mostly known to poses great potentials among major food crops for achieving break through that will improve food production in Nigeria (Nwabanne and

Igbokwe,2012). The husk and cobs are usually disposed as they are less significant to the farmer. Maize husk was therefore considered as adsorbents precursor for Pb^{2+} remediation from waste water since widely known methods are highly cost effective and inefficient in trace quantity removal (Hays, 2009). Hence, the need to develop less expensive techniques becomes unavoidable.

METHODOLOGY

All chemicals used were of analytical grade. Nitric Acid and lead nitrate (HNO_3 99% Assay and $Pb(NO_3)_2$) were obtained from Chemistry Laboratory of the Federal University of Technology, Minna. For column experiments, aqueous samples were pumped through the column with a peristaltic pump (Colperma-China). FT-IR(Shimadzu-8400S STIR China) was used in the determination of functional group present in the raw adsorbent. Scanning electron microscopy, SEM(Shimadzu-8200M, China)test was used to determine the microstructure while the residual heavy metal in the final effluent was determined using Atomic Adsorption Spectrophotometer, AAS(Shimadzu-4F8B23, China).

Preparation of Maize Husk Powder

Maize husk of approximately 5.0 Kg was collected from local farm along Gidan Kwano village in Minna, Niger State, Nigeria. They were cut into tiny pieces and washed thoroughly with tap water to remove any form of dirt.on the surface of the husk, then washed with distilled water, the wetted maize husks were sun dried to remove excess water and then oven dried at 60°C over night to remove any residual moisture. The dried maize husk was then crushed into smaller particles and segregated into particle sizes of 2000μm, 1000μm, 750μm and 500 μm using sieve, the sample was kept in an air tight container for further treatment. Chemical Treatment was used in this study due to

the low temperature required and ability to obtain higher pore with more enhanced porous structure in the treated adsorbent (Abia, 2007). The activating agent used is nitric acid (HNO₃). This reagent was chosen in this study based on the past researches conducted on similar lignocellulose precursors (Jude, 2007; Okonkwo *et al.*, 2012) and the results of using these chemical shows better pore formation in the adsorbent compared to others. The grinded sample was soaked in 2% v/v of nitric acid per 100grams of raw adsorbent for 18 hrs, the sample was sieved thereafter and washed severally with deionized water then dried at 50 °C for 12 hrs. It was then stored in a well isolated and tight container for further use.

Column experiments

A glass column of internal diameters (I.D) of 2.74 cmand 30 cm in length was used to adsorb Pb (II), a (6, 10 and 20 mgL⁻¹) of Pb (II) solution at flow rates of (1, 1.5 and 2.5 mLmin⁻¹) using column bed heights of (4, 8 and 12 cm). The base of the column was laid with glass wool before filling with treated maize husk. The top column was also covered with glass wool to prevent direct contact of the adsorbent with the effluent to be treated. All experiments were conducted at room temperature and the direction of flow was from top to bottom. The treated metal solution was collected at the outlet at time intervals of 2 hrs and analyzed using AAS. The column was run at a pre-determined pH of 5.5. The experimental conditions for the column runs are shown in Table 1.

Table 1: Experimental conditions for column runs

Column no	Flow rate (mL/min)	Concentration (mg/L)	Bed depth (cm)
1	1	6	12
2	1	6	8
3	1	6	4
4	1.5	6	4
5	2.5	6	4
6	1	20	4
7	1	10	4

Kinetic Model
The model used in this research was the Adams-Bohart model.

The Adams-Bohart model is used for the description of the initial part of the breakthrough curve. The fundamental equation describing the relation between effluent concentration to the influent concentration, C/Co and time in flowing systems was established by Adams and Bohart. Adams-Bohart model is used for the description of initial part of breakthrough curve and is given by the equation below with parameters Kab and No.

$$\frac{C}{C_o} = EXP\left(k_{ab}C_o t - k_{ab}N_o \frac{Z}{U_o}\right) \qquad 1$$

Where K_{ab} is the kinetic constant (l/mg min), U_o is the linear flow rate (ml/min), Z is the bed depth of column (cm), No is the saturation concentration (mg/L) and t is time (min).

RESULTS AND DISCUSSIONS
Functional composition (FT-IR)
Fourier transform infrared spectral analysis was carried out to identify the presence of various functional groups in

the adsorbent before and after adsorption. The functional groups which were recorded by the FT-IR includes the –OH- stretch, -CH- stretch, -C=C- stretch, -CN- stretch, -C=C-H- stretch as shown in Fig.1. FT-IR spectra of fresh and loaded adsorbent (maize husk) shows an intense and broad peak at 3565.94 cm^{-1} which can be attributed to the stretching of O-H group due to inter and intra molecular hydrogen bonding such as alcohols or phenols (Madhu *et al.*, 2014). Another peak observed at 3480.75 cm^{-1} can be associated with the stretching vibrations of N-H bond of amines (Nana and Maina 2010). C-H bond of methyl, methylene and methoxy groups was noticed at peak 3365.44 cm^{-1}. 2918.94 cm^{-1} peak was attributed to the =C-H associated with alkynes and aromatics (Dalia *et al*, 2014). The peaks around 1600-1033.90 cm^{-1} corresponded to the C=C stretching, N-O asymmetric stretch and C-N stretch which might be attributed to the presence of

aromatic or olefinic or N-H bending bands (Madhu *et al.*, 2014). The intense peak at 1000-400 cm^{-1} corresponded to the C-O stretching of alcohol or carboxylic acid (Ushakumary *et al.*, 2014).

FT-IR spectrum of the adsorbent with Pb (II) reveals that the peaks at 3565.49, 2918.94, 1455.77, 418.49 cm^{-1} (before adsorption) shifted slightly due to binding activity with lead (II) as shown in Fig 1. This was simply attributed to the participation of these functional groups in the binding of metal ions. It was also noted that shifting of wave number is dependent on the heavy metal concentration present in the sample and gross reduction in the transmittance could be attributed to adsorption activities (Madhu *et al.*, 2014). Table 2 shows comparison of FT-IR peaks and intensity positions of maize husk adsorbent before and after metal ions adsorption in wave number cm^{-1}.
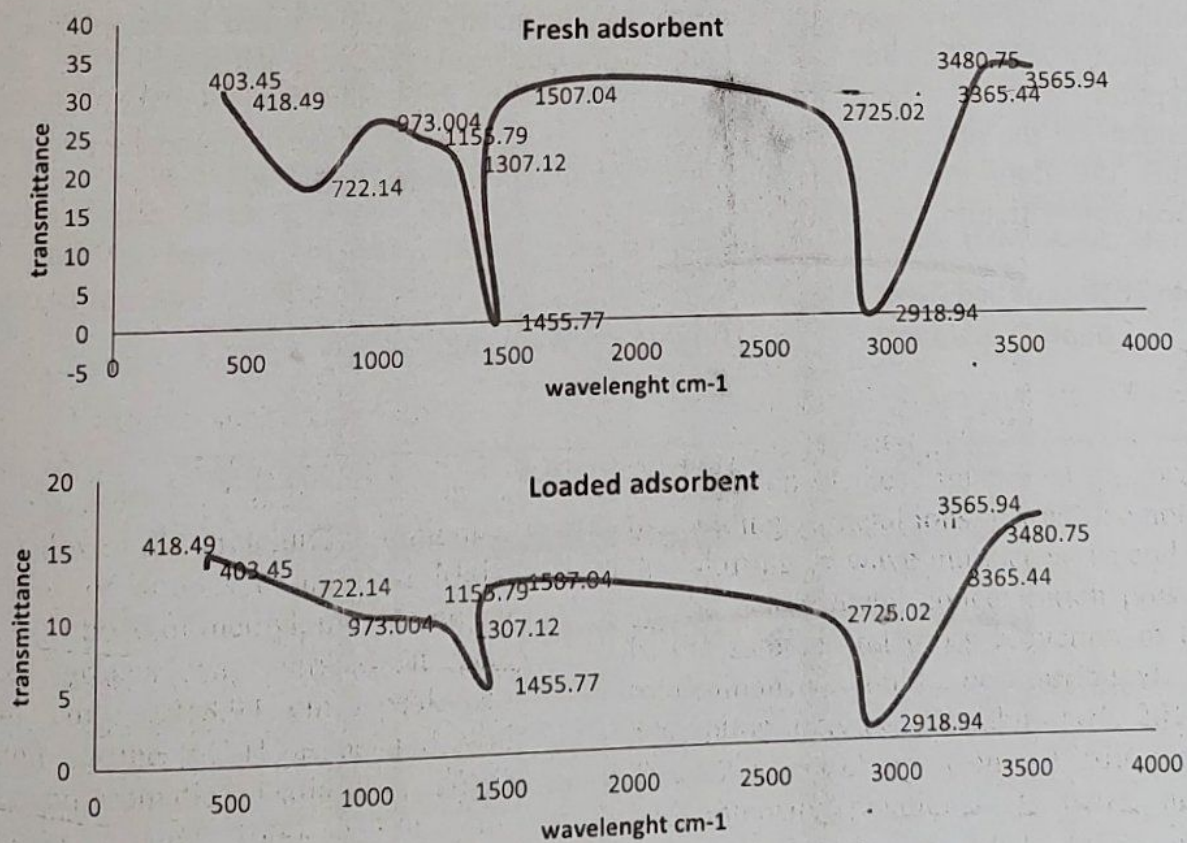
Fig 1. FT-IR Result of Fresh and Loaded Adsorbent

Surface Morphology

The result of scanning electron microscopy shows the morphology of the adsorbent before and after adsorption process(Berrin and Nagarajan, 2002). The presence of numerous pores which were observed in the adsorbent before adsorption with little patches of impurities within some pores which may be as a result of improper washing after treatment. Some pores were occupied by the adsorbate after the adsorption process as seen in Plate 1(Ushakumary et al., 2014).

Plate 1:SEM result for pore morphology of the adsorbent before and after adsorption

Column Efficiency

Column parameters are necessary to define the capacity and efficiency of the entire adsorption process. These are entirely dependent on the process variables which include the flow rate, initial and final effluent concentration, bed depth and time.

The parameters include the maximum adsorption capacity q_{max}, the uptake capacity q_{equ}, the metal loading W_{total} and the percentage removal %R.

Table 2, 3 and 4 shows the calculated values of the parameters using experimental variable.

Table 2Effect of bed depth

Bed depth (cm)	q_{total}(mg)	q_{equi}(mg/g)	W_{total}(mg)	%R
12	13.6665	1.08464	14.4	94.90625
8	13.6662	1.62693	14.4	94.90417
4	13.6516	3.17479	14.4	94.80292

Table 3Effect of flow rate

FlowRate (ml/min)	q_{total}(mg)	q_{equi}(mg/g)	W_{total}(mg)	%R
1.0	13.6516	3.17479	14.4	94.80292
1.5	20.4424	4.98595	21.6	94.64083
2.5	34.0333	7.91473	36.0	94.53708

Table 4Effect of concentration

InitialConc. (mg/L)	q_{total}(mg)	q_{equi}(mg/g)	W_{total}(mg)	%R
6	13.6516	03.17479	14.4	94.80292
20	45.0963	10.73721	48.0	93.95063
10	22.4406	05.21875	24.0	93.50275

Effect of bed depth

Fig 2 Show the breakthrough curves for varying bed depth with a constant flow rate and concentration of 1 ml/min and 6 mg/L respectively. From the breakthrough curve, a slight upshot of Pb (II) concentration was observed at bed depth of 4 cm, while at depth of 8 cm and 12 cm, the curve remain on the zero line, this implies that at 4 cm bed depth, the process is likely to have a shorter breakthrough time and hence achieve break through faster, this is because of the shorter residence time and binding force of the surface adsorbed while uptake capacity increased with increasing bed height. Generally, breakthrough time increases with increasing the bed height. As the bed height was increased, the Pb (II) had more time to contact with the adsorbent and hence resulted in higher removal efficiency of Pb (II) in the column. Higher bed depth results in a decrease in the solute concentration in the effluent at the same time. The slope of breakthrough curve tends to slightly decrease with increasing bed height (Okonkwo *et al.,* 2012)
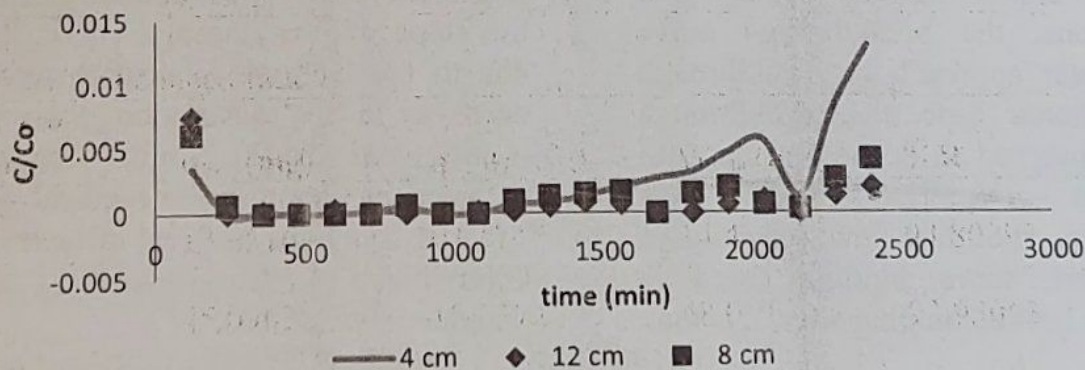

Fig 2:Breakthrough curve at varying bed height

Effect of flow rate

Fig 3 Show the breakthrough curves for varying flow rate with a constant bed depth and concentration of 4 cm and 6 mg/L respectively. The breakthrough curve for varying flow rate indicate a decrease in breakthrough time on the flow rate at 1.5 and 2.5 ml/min, this is observed by the slight rise in the breakthrough curve as against 1 ml/min curve. The shorter breakthrough time is attributed to increasing binding force and decrease in residence time and diffusion of the solute into the pores of the adsorbent, therefore the solute left the column before

equilibrium occurred. These results were in agreement with other findings. Ismail *et al.*, 2011 reported a breakthrough time of 1600 min for a high concentration and 1400 min for a high flow rate as against the total throughput time of 2100 min while using modified maize cub to remove Cr (IV) ion. It was generally observed that tendency of breakthrough occurred faster with higher flow rate. The reason is that at higher flow rate, the rate of mass transfer increased, thus the amount of Pb (II) adsorbed onto the bed height (mass transfer zone) increased (Nasehir *et al.*, 2011).
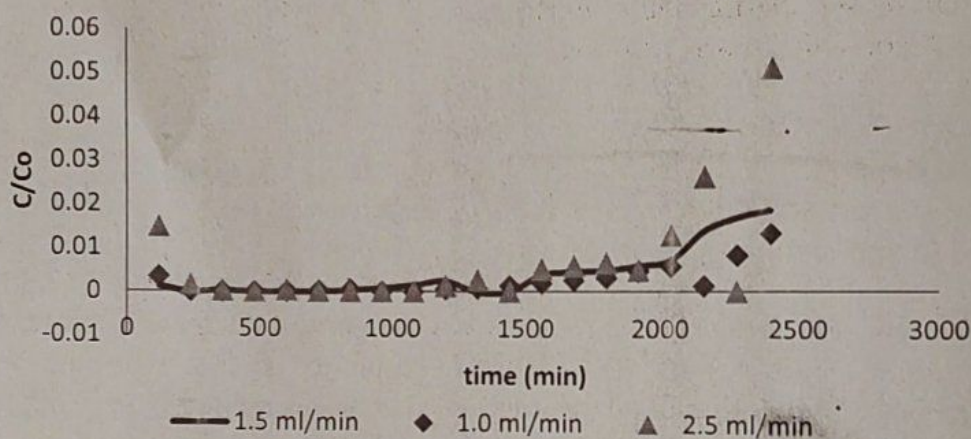
Fig 3:Breakthrough curves at varying flow rate

Effect of initial metal Ion concentrations

Fig 4 show the breakthrough curve for varying concentration with a constant bed depth and flow rate of 4 cm and 1 ml/min respectively It was observed that at higher concentrations, the breakthrough curve exhibits faster approach to breakthrough within a shorter time, the breakthrough time was observed to be decreasing with increase in concentration, this was attributed to the fact that at higher concentrations, more binding force is available for limited binding sites, this thus

leads to faster saturation of the column and thus effluent exit with substantial amount of residual heavy metal ion within a shorter period of time. Generally, the larger the inlet concentration, the steeper the slope of breakthrough curve. This is due to the increase in driving force and decrease in the adsorption zone length (Latiff *et al.*, 2011). Similar trends were obtained in literature for removal of lead (II) from synthetic and real effluents using immobilized *Pinussylvestris* sawdust (Fauduet *et al.*, 2005).

Fig. 4:breakthrough curves for varying initial metal concentration

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 (1) to the experimental data, a linear relationship was found for the time for breakthrough. For all breakthrough curves, respective values of N_o and k_{AB} were calculated and presented in Table 5. From the Table, it was ob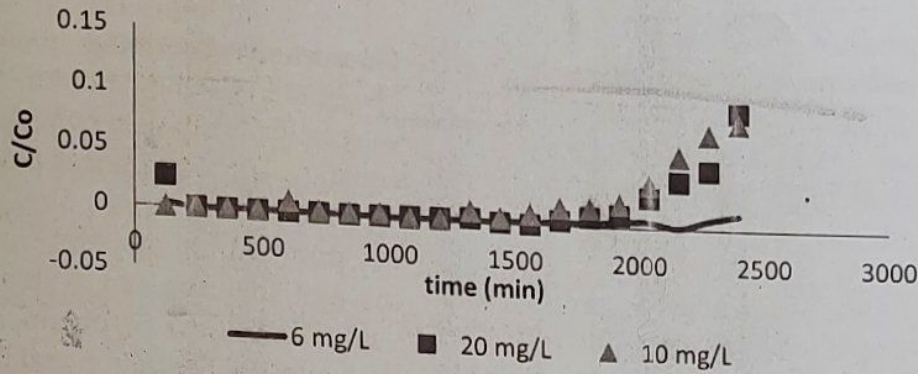served that the values of k_{AB} increased as the flow rate and the bed height increased and continued to increase with decrease in bed height. However, the

value of N_o 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. Since the acceptable threshold limit of Pb (II) ion in industrial effluent discharge stated by WHO, (2010) is 10 ppb Therefore, at $C_e = 0.001$ mg/L, service time (t) of 12, 16 and 24 hrs were obtained at a bed depth (H) of 4, 8 and 12 cm respectively. Therefore plotting t Vs. H gives the figure below

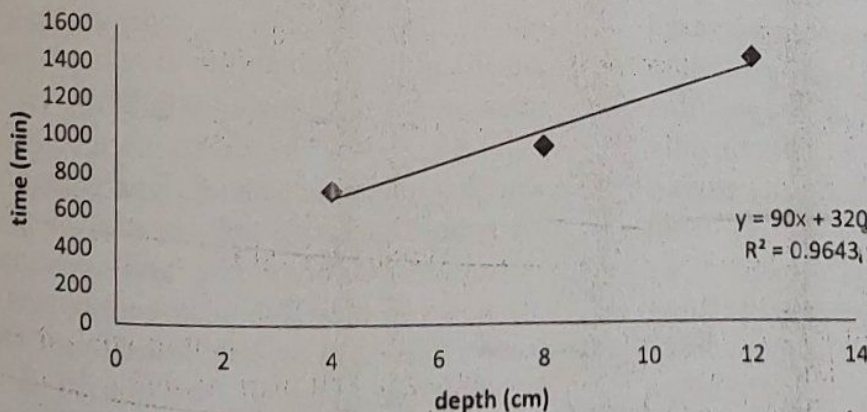$$y = 90x + 320$$
$$R^2 = 0.9643$$

Fig 5: Bed Depth Service Time

A high correlation coefficient observed above describes this model as a perfect tool for the theoretical determination of column parameters. From the above values

of slope and intercept, the Bed Depth Service Time proposed by Hutchins (1973) could be used to calculate the maximum uptake capacity of the column. The equation is given as

$$t = \frac{N_o}{Vc_o}Z - \frac{1}{k_b c_o}In\left(\frac{c_o}{c_e} - 1\right) \qquad (4)$$

Where slope $= \frac{N_o}{Vc_o}$ and

Intercept $= \frac{1}{K_b C_o} In\left(\frac{C_o}{C_e} - 1\right)$

From the above equation, N_o was calculated to be 0.522704 while K_b was 0.004531

Parameters describing the characteristic operations of the column (K_{ab} and No) were calculated using the linear form of equation 1. From a linear plot of $In(Ct/Co)$ against time (t), values of K_{ab} and N_o were determined from the intercept and slope of the plot for each run. Table 5 shows the values of K_{ab} and N_o obtained for different flow rate, concentration and bed dept.

Table 5: Adams-Bohart data parameters.

Bed depth (cm)	Flowrate (ml/min)	Initial Conc (mg/L)	Kab (mg^{-1}.min^{-1})	N$_o$theo (mg/g)	N$_o$exp (mg/g)
12	1	6	-3.3333E-05	0.697335	1.084643
8	1	6	-0.00005	0.447672	1.626929
4	1	6	-0.00005	0.241054	3.174795

From Table 5, it was observed that the values of N_o increased with increase in concentration and decrease with decrease in bed height. The values of K_{ab} decreased with increase in initial Pb(II) concentration as well as the flow rate. This showed that the overall system kinetics was dominantly external mass transfer in the initial part of adsorption in the column and this is in agreement with the result obtained by Ismail et al., (2011) and also in correlation with the experimentally obtained values of q_o (mg/g). The relatively low correlation coefficient explain non linearity since the bed did not attain saturation thus no breakthrough, the reason for this was earlier explained as due to insufficient throughput time.

CONCLUSION

Fixed column adsorption using treated maize peel to remove Pb (II) ion as carried out in this project work indicate that the adsorbent has high ability to remove heavy metal ions from aqueous solutions.

- The presence of various functional groups which include the carbonyl, amides, carboxyl etc. and appreciable pores in the fresh adsorbent as well as packed pore in the loaded adsorbent structure obtained from the FTIR and SEM analysis respectively revealed that maize husk is in fact an excellent adsorbent precursor.

- High efficiency in the use of this adsorbent is obtainable at lower flow

rate and influent concentration (higher resident time and binding sites). .

- Adsorption capacity strongly depends on flow rate, influent concentration, and bed height. The higher metal concentration and flow rate reduces the breakthrough time and percentage removal.

- Although the process was not completely achieved due to insufficient throughput time, the tendency for steeper mass transfer zones was noticed in the varied parameters.

- Comparison of the various kinetic models with experimental data was performed, and model parameters which were determined by linear regression analysis for Pb^{2+} adsorption under various operating conditions shows concurrence in the pattern through which the altered parameters affected the adsorption activities in the column. However, it was already established that when the breakthrough curve deviates from the ideal S shape, prediction derived from any model usually cannot meet our demand.

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