

# BIOREMEDIATION OF HEAVY METAL FROM WASTE WATER USING ACTIVATED MAIZE COB AS BIOSORBENT

**Author's name:** <sup>1</sup>Nwojo P. Enyinnaya, <sup>2</sup>Chidinma Q. Kanu

<sup>1</sup>Department of Pure and Industrial Chemistry, Faculty of Science, University of Port, Harcourt, Port Harcourt, Nigeria.

<sup>2</sup> Department of Pure and Industrial Chemistry, Faculty of Science, University of Port, Harcourt, Port Harcourt, Nigeria.

**Corresponding E-mail:** [nwojo.enyinnaya2@gmail.com](mailto:nwojo.enyinnaya2@gmail.com)

<b>Abstract</b>	<p>Activated maize cob (amc), an agro-waste was utilized as a biosorbent for the removal of <math>Pb^{2+}</math> and <math>Cu^{2+}</math> ions from simulated waste water. Batch experiments were conducted to determine the effects of varying contact time, initial metal ion concentration, adsorbent dosage, pH and temperature of adsorption on adsorption equilibrium capacity (<math>q_e</math>) and percentage removal (% R). % R increases with increasing adsorbent dosage for the two metal ions. It also increases with increase in temperature from 20°C to 60°C for <math>Cu^{2+}</math> but decreases with temperature increase for <math>Pb^{2+}</math> in the same range of temperature. The maximum adsorption of <math>Pb^{2+}</math> was found to be 95.65% at contact time of 20 minutes while that of <math>Cu^{2+}</math> was found to 93.97 % at contact time of 30 minutes. Thermodynamic parameters such as <math>\Delta H</math> and <math>\Delta S</math> were determined. <math>\Delta H</math> and <math>\Delta S</math> for <math>Pb^{2+}</math> were -32.26 KJ/mol and -79.50 J/mol/K respectively while those of <math>Cu^{2+}</math> were 22.88 KJ/mol and 92.12 J/mol/K respectively. The kinetics of the adsorption mechanism of <math>Cu^{2+}</math> and <math>Pb^{2+}</math> on the adsorbents was evaluated using Pseudo-first order rate, Pseudo-second order rate, Elovich equation, power function and intra-particle diffusion and film diffusion. The results show that Pseudo-second order model provides a more appropriate description of the metal ions adsorption. Adsorption isotherms were determined and correlated using Langmuir, Freundlich, Harkins and Jura, Temkin, Halsey and Dubinnim-Radushkevich models. These morphological investigations by FTIR and SEM analysis showed that activated maize cob has active pores and ionisable functional groups at the surface which enhance its adsorption capacity. It is therefore concluded that locally available maize cob can be activated and used as sorbent for heavy metals (<math>Pb^{2+}</math> and <math>Cu^{2+}</math>) removal, representing an effective and environmentally clean utilization of waste matter.</p>
<b>Keywords</b>	Copper, lead, activated maize cob, adsorption.

## INTRODUCTION

Water pollution due to the presence of heavy metals in water and wastewaters has been a major cause of concern for environmental scientists and engineers. Rapid industrialization and urbanization have resulted in the generation of large quantities of aqueous effluents, many of which contain high levels of toxic pollutants (Krishnani et. al.2004). Several episodes of heavy metal contamination in aquatic environment have increased the awareness about heavy metal toxicity (Upendra, 2006). Among these, Minamata tragedy due to Mercury poisoning and “Itai-Itai” disease in Japan due to cadmium toxicity are well known (Upendra, 2006). Few years back, cases of lead poisoning were reported in Zamfara State, Nigeria; which led to the death of several people and animals as a result of lead contamination of water bodies (streams and rivers) and the environment (Sadeeq, 2010 and Isah, 2010). Various physicochemical and biological processes are usually employed to remove pollutants from industrial waste water before discharge into the environment. In case of treatment of adsorptive pollutants like heavy metals and ionic dyes, however, most of the conventional treatment processes, especially chemical precipitation or coagulation, become less effective and more expensive when the adsorbates are in a low concentration range (Crini 2006). Although ion exchange resins and

activated carbons have long been recognized as effective commercial adsorbents for treating industrial waste water containing adsorptive pollutants, their high cost and low efficiency have limited their commercial use in actual industrial scenario (Aydin et. al., 2008). The presence of heavy metals in the environment is thus of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentration (Okuo and Ozioko (2001); Malakul, et.al, 2002; Mohan and Singh, 2002).

## MATERIALS AND METHODS

### *Collection and preparation of maize cob (Biosorbent)*

Maize cob wastes were collected from a garden farm land in Abiriba in Ohafia LGA of Abia state, Nigeria. The maize cob wastes were properly washed with running water from tap to remove any dirt and other particulate matter that might interact with any sorbed metal ions. This was followed by washing with distilled water and sundry for some days. The dried samples were ground and sieved using 40-80nm sieve. The samples were stored in separate plastic air tight containers for further analysis. The sample was activated with phosphoric acid by mixing maize cob and phosphoric acid (14.8 M  $H_3PO_4$ ) in the volume ratio of 1:3 and kept for 24 hours. After 24 hours, the soaked maize cob was washed severally with distilled water. The acidity of the sample was repeatedly monitored until the pH reading was within the range of 6-7 (that is almost neutral). The sample was then dried again and used for the analysis.

### *Preparation of heavy metal solutions (Sorbate)*

Stock solution of  $Cu^{2+}$  ion was prepared by weighing 3.80 g of  $Cu(NO_3)_2 \cdot 3H_2O$  into 1 litre (1000 ml) volumetric flask and make up with distilled water to have 1000 mg/L  $Cu^{2+}$  ion concentration in solution. Stock solution of  $Pb^{2+}$  ion was prepared by weighing 1.60 g of  $Pb(NO_3)_2$  into 1 litre (1000 ml) volumetric flask and make up with distilled water to have 1000 mg/L  $Pb^{2+}$  ion concentration in solution. The experimental solutions were prepared by diluting definite volume of the stock solutions to get the desired concentrations.

### *Batch Adsorption Experiments*

The experiment for the removal of the copper and lead from aqueous waste was conducted in 250 ml air tight Erlenmeyer flask by taking 100 ml of a known concentration of the heavy metal solution at room temperature. For each run, weighed amount of adsorbent was placed in the flask and agitated on a mechanical shaker at 150 revolution/minutes. The effect of contact time (15, 20, 30, 40, 50, 60 and 70 minutes), adsorbent dosage (2, 4, 6, 8, and 10 g), initial concentration of (50, 100, 150, 200 and 250 mg/L), pH (2, 4, 6, 8, 10 and 12) and temperature (293, 303, 313, 323 and 333 K) were studied. The flask containing the samples were withdrawn from the shaker at predetermined time intervals, filtered and the final concentrations of metal ions in the supernatant solutions were analyzed using the Atomic absorption spectrophotometer (AAS) (Model Perkin Elmer A Analyst 200). The pH of the solution was adjusted using 1M HCl or NaOH. All experiments were performed in duplicate and the mean value reported. Percentage removal of the heavy metal by the adsorbent during the experiments was calculated using the formula

$$\% \text{ Removal} = \left( \frac{C_o - C_e}{C_o} \right) \times 100\% \quad 1$$

The amount of heavy metal adsorbed per unit weight of adsorbent at equilibrium will be calculated as  $q_e = \left( \frac{C_o - C_e}{w} \right) V$  2

Where  $C_o$  and  $C_e$  are initial and equilibrium concentrations of heavy metal ions respectively.  $V$  is the volume (L) of experimental solution and  $w$  is the mass (g) of the adsorbent used.

## ADSORBENT CHARACTERIZATION

Surface morphology of the activated maize cob was analyzed using scanning electron microscope

(SEM) (Model-PHENOM ProX). Prior to scanning, some quantity of the adsorbent was placed on a double adhesive sticker placed in a sputter machine for 5 sec; this gave the adsorbent a conductive property. Sample (adsorbent) stud was fixed on a charge reduction sample holder, and then was charged in the SEM machine. The Fourier transform Infra-red (FTIR) analysis of activated maize cob was carried out by a FTIR spectrophotometer (Shimadzu-8400S). For sample analysis, 0.5 g of each sample was mixed with about the same amount of potassium bromide KBr. The mixture thus obtained was crushed in a mortar to obtain a homogeneous powder which was then introduced into a mould to obtain very fine plates. The plates were then introduced into the spectrophotometer for analysis. The wave number was found to vary between 4000 and 450 cm<sup>-1</sup>. FTIR study was used to identify the different functional groups (active sites) available on the adsorbents.

**THEORY**

**Thermodynamics Studies**

Van't Hoff and Gibb's free energy equations were used to study the effect of adsorption of metal ions (Cu<sup>2+</sup> and Pb<sup>2+</sup>) on activated maize cob. From the study of the temperature dependence of metal ions biosorption on activated maize cob, the free energy change ΔG, enthalpy change ΔH and entropy change ΔS was determined. Assuming that the activity coefficients are unity at low concentration, the apparent equilibrium constant K'<sub>c</sub> of the biosorption is defined as [Aksu 2002 and Han et al. 2005]

$$K'_c = \frac{C_{ad,e}}{C_e} = \frac{C_o - C_e}{C_o} \quad 3$$

Where C<sub>o</sub> = initial metal ion concentration, C<sub>ad,e</sub> = the metal ion concentration on the adsorbent at equilibrium and C<sub>e</sub> = concentration of the metal ion at equilibrium.

The K'<sub>c</sub> value is used in the equation below to determined the Gibb's free energy ΔG of biosorption

$$\Delta G = -RT \ln K'_c \quad 4$$

The Gibbs free energy equation is given by

$$\Delta G = \Delta H - T\Delta S \quad 5$$

Combining equations 3 and 4 and rearranging, we obtain the Van't Hoff equation;

$$\ln K'_c = \left\{ -\frac{\Delta H}{R} \right\} \frac{1}{T} + \frac{\Delta S}{R} \quad 6$$

The enthalpy change ΔH and the entropy change ΔS can be obtained from the slope and intercept of the Van't Hoff plot of lnK'<sub>c</sub> against 1/T or the Gibbs plot of ΔG against T.

**ADSORPTION KINETICS**

Adsorption kinetics were studied using Pseudo first order, pseudo-second order, power function, Elovich model, intra-particle diffusion model and Boyd kinetic model.

**PSEUDO-FIRST ORDER MODEL**

The simplified linear form of pseudo first order kinetic equation of Lagergren model based on equilibrium adsorption is expressed as

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log q_e \quad 7$$

**PSEUDO-SECOND ORDER MODEL**

This can be linearised pseudo second order equation

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{q_e^2 k_2} \quad 8$$

Here k<sub>2</sub> is the rate constant (min g/mg) of second order adsorption. The linear plot of  $\frac{t}{q_t}$  versus t gave  $\frac{1}{q_e}$  as slope and  $\frac{1}{q_e^2 k_2}$  as intercept for adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions onto the adsorbent.

The value of  $k_2$  ( $\text{min}^{-1}\text{g}/\text{mg}$ ) can be calculated from the intercept  $\frac{1}{q_e^2 k_2}$  while  $q_e$  can be calculated from the slope. The initial sorption rate  $h$ , is given by

$$h = q_e^2 k_2 \quad 9$$

The rate constant  $k_2$ , initial sorption rate  $h$ , and predicted  $q_e$  can be calculated from the plot of  $\frac{t}{q_t}$  versus time  $t$ .

### POWER FUNCTION KINETIC MODEL

The equation of power function kinetic model is given by

$$\log q_t = b \log t + \log a \quad 10$$

where **a** is initial rate and **b** is the rate constant. A plot of  $\log q_t$  versus  $\log t$  yield a straight line graph with a slope of **b** and intercept of **log a**.

#### 3.2.4 Elovich Kinetic model

The Elovich equation (sparks 1986) is generally given by

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad 11$$

where  $\alpha$  is the initial adsorption rate ( $\text{mg}/\text{g}$ ) and  $\beta$  is the rate constant ( $\text{mg}/\text{g}/\text{min}$ ) during any one experiment. A plot of  $q_t$  versus  $\ln t$  yield a linear relationship with a slope of  $\frac{1}{\beta}$  and intersect of  $\frac{1}{\beta} \ln(\alpha\beta)$  if the sorption process fits the Elovich equation.

### INTRA-PARTICLE AND FILM DIFFUSION KINETICS

The basic assumption with intra-particle diffusion model is that film diffusion is negligible and intra-particle diffusion is the rate determining step (Venkata et al. 2008). According to Weber and Morris (1963), if the rate limiting step is the intra-particle diffusion, then the amount adsorbed at any time  $t$  should be directly proportional to the square root of contact time  $t$  and shall pass through the origin. This is defined mathematically as

$$q_t = K_{id} t^{0.5} \quad 12$$

where  $q_t$  ( $\text{mg}/\text{g}$ ) is the amount adsorbed at time  $t$  ( $\text{min.}$ ) and  $k_{id}$  ( $\text{mg}/\text{g}/\text{min}^{0.5}$ ) is the intra-particle rate constant. The slope of the plot gives  $K_{id}$  while the intercept is  $C$ , the boundary layer effect. The larger the intercept observed, the greater will be the contribution of the surface sorption in the rate controlling step.

### BOYD KINETIC MODEL

Due to the double nature of intra-particle diffusion (both film and pore diffusion), and in order to determine the actual rate controlling step involved in the adsorption process, the kinetic data were further analysed by using Boyd kinetic equation (Boyd et al. 1947) expressed as

$$F = \frac{6}{\pi^2} \exp(-Bt) \quad 13$$

$$\text{and } F = \frac{q}{q_e} \quad 14$$

where  $q_e$  is the amount of metal ion adsorbed at equilibrium ( $\text{mg}/\text{g}$ ) and  $q$  represents the amount of metal ion adsorbed at any time  $t$  ( $\text{min}$ ),  $F$  represent the fraction of metal ion adsorbed at any time  $t$ , and  $Bt$  is the mathematical function of  $F$ . Equation above can be rearranged and given by

$$Bt = -0.4977 - \ln(1-F) \quad 15$$

The plot of  $[-0.4977 - \ln(1-F)]$  against  $t$  was employed to test the linearity of the experimental data. A straight line passing through the origin is an indication of adsorption processes governed by particle diffusion mechanism; otherwise they are governed by film diffusion (Mohan and Singh 2002).

**ADSORPTION ISOTHERM**

The experimental data for the uptake of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions by activated maize cob over the studied concentration range were processed in accordance to the following isotherms: Langmuir, Freundlich, Harkins and Jura, Halsey, Temkin and Dubinnin- Radushkevich isotherms.

**LANGMUIR ISOTHERM**

This model suggests that the sorption occurs on homogenous surface by monolayer sorption without interaction between the sorbed molecules. The model assumes uniform energies of adsorption onto the surface. It is valid for monolayer sorption on a surface containing finite number of binding site and no transmigration of sorbate in the plane of the surface.

The linearised Langmuir isotherm equation is given by

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}} C_e \quad 16$$

where  $q_{max}$  is the maximum metal ions uptake per unit mass of adsorbent (mg/g), which is related to the adsorption capacity,  $K_L$  is Langmuir adsorption constant (L/mg) and is related to the measure of affinity of adsorbate for the adsorbent,  $C_e$  is the metal ion residual concentration in solution,  $q_e$  is equilibrium metal ion concentration on the adsorbent (mg/g). A plot of  $\frac{C_e}{q_e}$  versus  $C_e$  yields a straight-line graph which has an intercept and slope which correspond to  $\frac{1}{q_{max}K_L}$  and  $\frac{1}{q_{max}}$  respectively, from where  $q_{max}$  and  $K_L$  can be calculated. To confirm the favorability of an adsorption process to Langmuir isotherm, the essential features of the isotherm can be expressed in terms of a dimensionless constant called separation factor or parameter  $R_L$  which can be calculated as

$$R_L = \frac{1}{1+K_L C_o} \quad 17$$

where  $C_o$  is the highest initial adsorbate concentration (mg/g). The value of  $R_L$  indicates whether the isotherm is irreversible ( $R_L=0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ) (Kadirvelu and Namasivayam 2003).

**FREUNDLICH ISOTHERM**

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption representing heterogenous surface properties. This isotherm is linearised as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad 18$$

where  $q_e$  = solid phase concentration in equilibrium  
 $C_e$  = liquid phase metal ion concentration at equilibrium,  
 $\frac{1}{n}$  = intensity adsorption (heterogeneity factor)  
 $K_f$  = Freundlich constant (multilayer adsorption capacity)

The magnitude of  $n$  gives an indication of the favourability of adsorption. It is generally stated that the value of  $n$  in the range 2-10 represent good, 1-2 moderately good and less than 1 poor adsorption characteristics (Aksu and Kutsal 1991). A plot of  $\log q_e$  versus  $\log C_e$  gives a straight line. The values of  $n$  and  $K_f$  are determined from the slope and intercept of the graph.

**HARKINS AND JURA ISOTHERM**

The Harkins and Jura isotherm can be expressed as (Bazar 2006, Harkins and Jura 1944) as

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e \quad 19$$

The isotherm equation accounts for multilayer adsorption and can be explained by the existence

of a heterogeneous pore distribution. The Harkins-Jura isotherm parameters were obtained from the plots of  $\frac{1}{q_e}$  against  $\log C_e$ . These yields a straight line graph which has slope and intercepts which correspond to  $-\frac{1}{A}$  and  $\frac{B}{A}$  respectively.

**HALSEY ISOTHERM**

Halsey proposed an expression for condensation of a multilayer which can be linearised as:  

$$\ln q_e = \frac{1}{n_H} \ln K_H - \frac{1}{n_H} \ln C_e \tag{20}$$

This equation is suitable for multilayer adsorption. A plot of  $\ln q_e$  versus  $\ln C_e$  yields slope and intercept which corresponds to  $-\frac{1}{n_H}$  and  $\frac{1}{n_H} \ln K_H$  respectively.

**TEMKIN ISOTHERM**

Temkin and Pyzhev (1940) studied the heat of adsorption and the adsorbent-adsorbate interaction on the surfaces. The Temkin isotherm equation is given as

$$q_e = B \ln K_T + B \ln C_e \tag{21}$$

Where  $B = \frac{RT}{b}$ , T (K) is the absolute temperature, R is the universal gas constant (8.314J/mol),  $K_T$  is the equilibrium binding constant or adsorption potential (L/mg),  $q_e$  (mg/g) and  $C_e$ (mg/L) are the amount of adsorbed at equilibrium and equilibrium concentration respectively, and B is related to the heat of adsorption (kJ/mol). A linear plot of  $q_e$  versus  $\ln C_e$  describes the Temkin isotherm for the adsorption of the metal ions ( $Cu^{2+}$  and  $Pb^{2+}$ ) onto the activated maize cob adsorbent. The Temkin constants B and  $K_T$  were determined from the slope and intercept of the linear plots respectively.

**DUBININ-RADUSHKEVICH (D-R) ISOTHERM**

Characteristics of adsorption can also be studied by applying the Dubinin- Radushkevich (D-R) model whose linear form is written as

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{22}$$

where  $q_m$  = maximum adsorption capacity (mg/g),

$\beta$  = activity coefficient ( $\text{mol}^2/\text{J}^2$ ), R = gas constant (8.314 J/mol/K),

T = temperature in Kelvin (K),  $\varepsilon$  = Polanyi or adsorptive potential.

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \tag{23}$$

$\beta$  was further used to calculate the mean free adsorption energy E(kJ/mol) using the equation

$$E = \frac{1}{\sqrt{2} \beta} \tag{24}$$

The values of  $q_m$ ,  $\beta$  and E for adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  ions onto the adsorbent were obtained from the linear plot of  $\ln q_e$  versus  $\varepsilon^2$ . The slope represents  $-\beta$  while the intercept represents  $\ln q_m$ .

**RESULTS AND DISCUSSION**

**Adsorbent characterization**

**Scanning Electron Microscopy (SEM) STUDY**

Scanning electron microscopy (SEM) gives the morphological evidence of amc which is shown in Fig 1a-1c. Significant number of pores was observed in amc structure. Due to the well-developed active pore spaces created by phosphoric acid activation, activated maize cob had high surface area and high porosity resulting in its greater adsorption capacity. This makes it a very good biosorbent for adsorptive removal of heavy metals from aqueous wastewater.

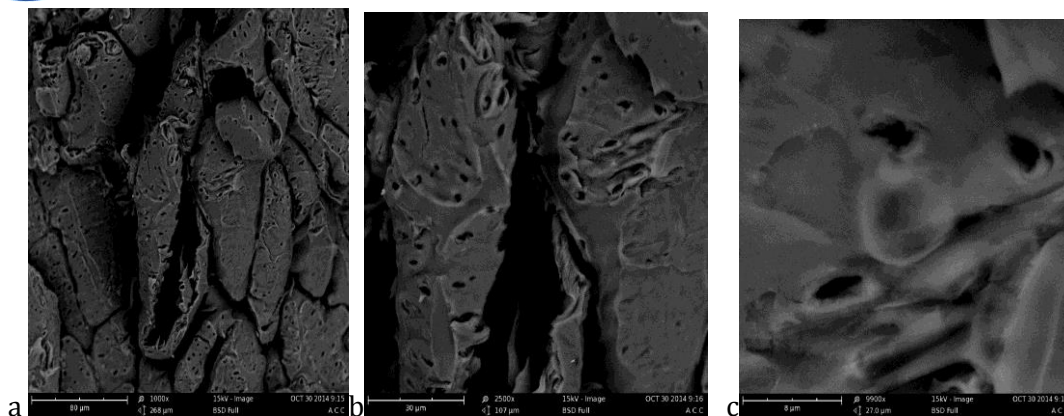


Fig. 1 Scanning electron microscopy (SEM) of activated Maize Cob (a) 1000x (b) 2500x (c) 9900x

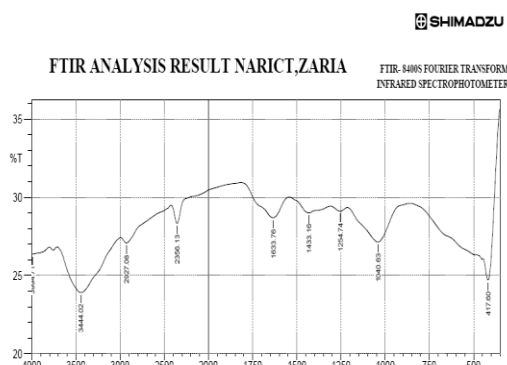
**Fourier Transformation Infrared (FTIR) Study**

The FTIR spectroscopy is a well known method for identification of functional groups and quantitative analysis of samples. In order to gain better insight into the surface functional groups available on the surface of the adsorbents, its FTIR spectrum was recorded as shown in Fig 2.

When compared to the FTIR spectra of raw maize cob (Okorocho et. al. 2019), It is quite clear from the spectra that some peaks shifted due to activation and some others disappeared after the treatment with phosphoric acid. The peaks at 1040.63  $\text{cm}^{-1}$  and 1257.74  $\text{cm}^{-1}$  represent C-O stretching in alcohol, phenols, esters or the P=O in phosphate esters. The absorption bands at 1433.16  $\text{cm}^{-1}$  and 1633.76  $\text{cm}^{-1}$  show the C-H asymmetric bending and the C=C alkene/ aromatic skeletal stretching respectively. 2356.13  $\text{cm}^{-1}$  band is attributed to  $\text{C}\equiv\text{N}$ . The peaks at 2927.08  $\text{cm}^{-1}$  and 3444.02  $\text{cm}^{-1}$  are due to C-H stretching and O-H stretching (from carboxylic acid and alcohols)/N-H (from amine or amide) respectively. The O-H and N-H groups are responsible for intermolecular hydrogen bonding on the surface. 3994.71  $\text{cm}^{-1}$  peak is due to C-H terminal alkyne.

**Table 1: some fundamental functional groups on activated maize cob**

Band position ( $\text{cm}^{-1}$ )	Bonds/functional group
1040.63	C-O stretching from carboxylic acid, alcohol
1254.74	C-O from phenol, esters, P=O in phosphate esters
1433.16	C-H asymmetric bending from alkane
1633.76	C=C from alkene/aromatic ring
2356.13	$\text{C}\equiv\text{N}$ stretching from nitrile
2927.08	C-H stretching
3444.02	O-H stretching from carboxylic acid/alcohol
3994.71	C-H from terminal alkyne



**Fig.2: FTIR spectra of activated maize cob (amc) EQUILIBRIUM STUDIES**

**4.2.1 Effect of contact time**

The time taken to attain equilibrium for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  at neutral pH, temperature of 27°C and moderate speed at 150 rpm using 2 g of activated maize cob is shown in Fig 3. The percentage removal of  $\text{Pb}^{2+}$  by the adsorbent increases and attains equilibrium at 20 minutes while that of

$\text{Cu}^{2+}$  increases and attains equilibrium at 30 minutes respectively after which desorption takes

place in both cases. The results show that maximum adsorption of both metals ion was achieved at a lower contact time for the activated maize cob. This is because activating an adsorbent helps to open up the pores (active sites) where adsorption takes place (Chowdhury *et al.*, 2011a). The decrease in percentage removal of metal ion after reaching the maximum adsorption may be due to the saturation of adsorption sites of the adsorbents with the metal ions (Chowdhury *et al.*, 2011b). It may also be due to the breakage of newly formed weak adsorption bonds due to constant agitation.

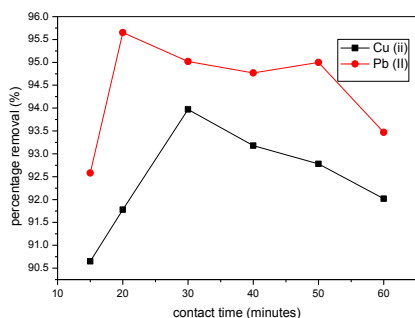


Fig. 3: Effect of contact time on adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> onto activated maize cob

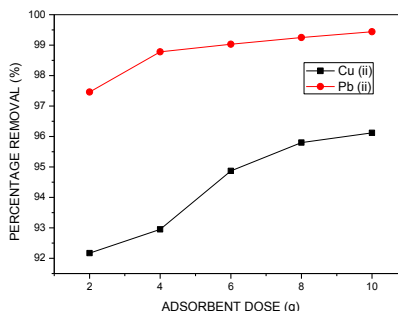


Fig. 4: Effect of adsorbent dosage on adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> onto activated maize cob

### EFFECT OF ADSORBENT DOSAGE

The effects of dosage of the adsorbent on Cu<sup>2+</sup> and Pb<sup>2+</sup> are shown in Fig. 4. The dependence of Cu<sup>2+</sup> and Pb<sup>2+</sup> sorption on the adsorbent dosage was studied by varying the amount of adsorbent dose while keeping other parameters (pH, temperature, concentration of metal ion and contact time) constant. It can be inferred that percentage removal for both metal ions increases with increase in adsorbent dosage from 2 g to 10 g. The increase in Cu<sup>2+</sup> and Pb<sup>2+</sup> percentage removal with increase in adsorbent dose is due to the greater availability of the exchangeable sites or surface area and functional groups at higher dosage (Namasivayan *et al.*, 1998 and Garg *et al.*, 2007). These functional groups were important in the formation of Van der waals bonding which play a major role in binding metals to the adsorbent during adsorption process. Because of increase in the adsorbent dosage, the amount of metal ions adsorbed per unit mass (q<sub>e</sub>) decreases (Garg *et al.*, 2007).

### EFFECT OF INITIAL CONCENTRATION OF ADSORBATE

The effect of initial concentration of adsorbate (Cu<sup>2+</sup> and Pb<sup>2+</sup>) on the adsorbent is shown in Fig.5. The initial concentration provides a driving force to overcome all mass transfer resistances of the metal ions in aqueous and solid phase (Malkoc *et al.* 2005). The amount of metal ion adsorbed increases with increase in initial metal ion concentration. The results showed that initial concentration of the metal ions (Cu<sup>2+</sup> and Pb<sup>2+</sup>) increases as the amount of metal ion adsorbed increases for the adsorbent. For an increase in initial concentration of metal ions from 50 to 250 mg/L, the amount of Cu<sup>2+</sup> adsorbed increases from 2.417 to 11.076 mg/g while for Pb<sup>2+</sup> it increases from 2.472 to 11.127 mg/g. The increase in amount of metal adsorbed (adsorption capacity) is due to the higher adsorption rate and the utilization of active sites available for the adsorption at higher concentration (Siti *et al.*, 2013).

### EFFECT OF PH

The effects of pH on the adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> onto adsorbents are shown in Fig.6. The effect of solution pH on biosorption could be related to the active sites (surface functional groups on the biomass cell walls) and also to the chemistry of the solute in the solution. The percentage removal of Cu<sup>2+</sup> and Pb<sup>2+</sup> for the adsorbent increases with increasing pH from 2 to 12.



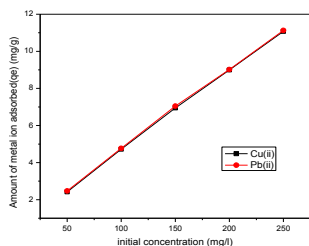


Fig.5: Effect of initial concentration of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  onto activated maize cob

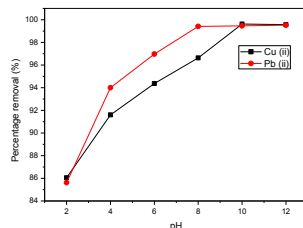


Fig.6: Effect of pH on the activated maize cob adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by amc

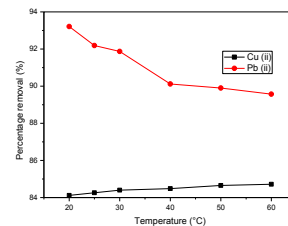


Fig.7: Effect of temperature on

This is because at lower pH, the overall surface charge on the adsorbent will be positive, which will inhibit the approach of positively charged metal cations, consequently reducing metal ion binding on the adsorbent surface. At lower pH, the  $\text{H}^+$  ions compete effectively with the metal ions causing a decrease in adsorption capacity and percentage removal. At higher pH, the adsorbent surface is negatively charged thereby encouraging more metal ion uptake due to the electrostatic forces of attraction between the negatively charged adsorbent surface and the positively charged metal ion. This is consistent with the observation of Lisa et al. 2004 and Xiao et al. 2009.

### EFFECT OF TEMPERATURE

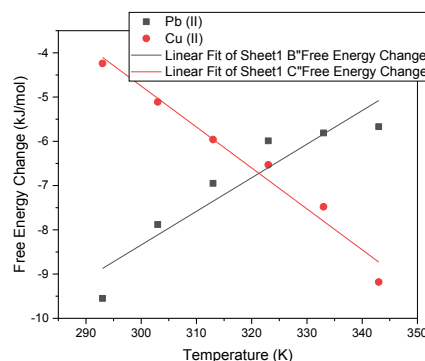
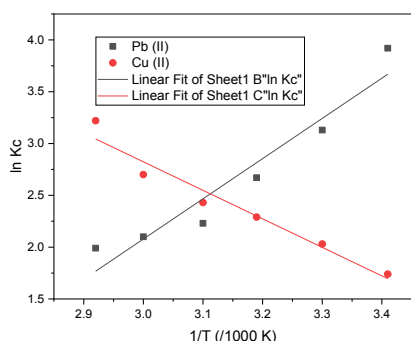
The effects of temperature on the adsorption of metal ions onto the bio sorbents are shown in Fig.7. The percentage removal as well as adsorption capacity of  $\text{Cu}^{2+}$  increases with increase in temperature. This is because increase in temperature results in widening of pores on the active sites of the adsorbent which create more room for greater adsorption. Increase in adsorption with temperature may also be due to the increase in number of active adsorption sites (Domenico and Schwartz 1990) generated as a result of breaking of some internal bonds near edge of active sites in the adsorbents (Pandey et al. 1986). The increase showed that the adsorption of  $\text{Cu}^{2+}$  ions by activated maize cob is endothermic. The percentage removal as well as adsorption capacity of  $\text{Pb}^{2+}$  decreases with increase in temperature. Decrease in adsorption capacity for  $\text{Pb}^{2+}$  at higher temperature may be due to the damage of active binding sites in the biomass (Ajmal et al., 2003). It may equally be due to the fact that increase in temperature leads to increase in kinetic energy of  $\text{Pb}^{2+}$  ions and therefore weakening of the forces of attraction between the  $\text{Pb}^{2+}$  ions and the adsorbents. This results in decrease in percentage removal and adsorption capacity. The decrease revealed that the process of adsorption for  $\text{Pb}^{2+}$  ions by activated maize cob is exothermic (sag and Kutsal, 2000).

### THERMODYNAMICS STUDIES

van't Hoff and Gibb's free energy equations were used to study the effect of adsorption of metal ions ( $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ) on activated maize cob are shown in Fig.8 and Fig.9. The enthalpy change  $\Delta H$  and the entropy change  $\Delta S$  can be obtained from the slope and intercept of the van't Hoff plot of  $\ln K'_c$  against  $1/T$  or the Gibbs plot of  $\Delta G$  against  $T$ . The negative values of Gibbs freeenergy change  $\Delta G$  at various temperatures suggest that the adsorption is rapid and feasible. This could be an explanation for high metal binding capacity shown by the adsorbents. The negative value of  $\Delta G$  (table 2) decreases with temperature, indicating that the spontaneous nature of  $\text{Cu}^{2+}$  ion bio sorption is inversely proportional to the temperature (Han 2005 and Aksu 2002). The values of enthalpy change  $\Delta H$  and entropy change  $\Delta S$  obtained for adsorption of  $\text{Cu}^{2+}$  ions onto activated maize cob is 22.88kJ/mol and 92.12 respectively as can be seen in table 2. The positive value of  $\Delta H$  confirms the endothermic process of adsorption (sag and Kutsal, 2000). This result is also supported by the increase in the value of adsorption capacity of

adsorbent with the rise in temperature. The increasing sorption capacity of the adsorbent with temperature is due to the enlargement of pores and/or the activation of the adsorbent surface (Han 2006). Additionally, positive value of  $\Delta S$  shows the increased degree of free active sites at the solid-liquid interface during the adsorption process.

However, for the biosorption of  $Pb^{2+}$  ions onto the adsorbent, the values of enthalpy change  $\Delta H$  and entropy change  $\Delta S$  are both negative (table 2). The negative values of  $\Delta H$  indicated the exothermic behaviour of the reaction. This shows that the interaction of  $Pb^{2+}$  ions onto the adsorbents is an energetically stable exothermic process and that adsorption occurred through a bonding mechanism (Rounak sharrif et al. 2011 and Elsayed et al. 2007). The negative values for  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  of  $Pb^{2+}$  ions confirmed that the adsorption processes proceed more at lower temperature and done via enthalpy effect.



(Fig.8: Van't Hoff plot of adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  on amc) (Fig.9: Gibb's plot of adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  on amc)

Table 2: Thermodynamic parameters of adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  onto amc

Temperature (K)	1/Temperature (K <sup>-1</sup> )	ln K <sub>c</sub>	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)
$Pb^{2+}$					
293	0.00341	3.92	-9.55	-32.26	-79.50
303	0.00330	3.13	-7.88		
313	0.00319	2.67	-6.95		
323	0.00310	2.23	-5.99		
333	0.00300	2.10	-5.81		
343	0.00292	1.99	-5.67		
$Cu^{2+}$					
293	0.00341	1.74	-4.24	22.88	92.12
303	0.00330	2.03	5.11		
313	0.00319	2.29	-5.96		
323	0.00310	2.43	-6.53		
333	0.00300	2.70	-7.48		
343	0.00292	3.22	-9.18		

### ADSORPTION KINETICS STUDIES

Pseudo first order model did not provide a good fit to the experimental data as seen in the low value of  $R^2$  in table 3. Equally, the theoretical and experimental equilibrium adsorption capacity  $q_e$  differs considerably thus confirming the inability of pseudo first order in explaining the adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  onto activated maize cob.

Pseudo second order kinetic model provides a good fit with high  $R^2$  values (Kumar and Porkodi, 2007) of 0.999 (table 3) for each metal ion and linearity of the plot (Fig.10). In addition, there is good correlation between the theoretical and experimental adsorption capacity, thus confirming that the adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  onto activated maize cob followed pseudo second order model. This suggests that the metal uptake process is due to chemisorption which can occur by the polar functional groups of lignin which include alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers as chemical bonding agents (Ho and Mckay, 1999, Ho 2003, Vadivelan et

al. 2005). A similar result was previously reported by Ho (2003), Chowdhury et. al (2010), and Okorochoa et. al. (2019) for Cu<sup>2+</sup> onto tree fern adsorbent, Pb<sup>2+</sup> ion onto palm oil fuel ash POFA and respectively Cu<sup>2+</sup> and Pb<sup>2+</sup> onto raw maize cob (rmc).

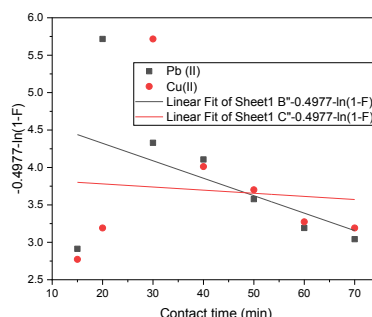
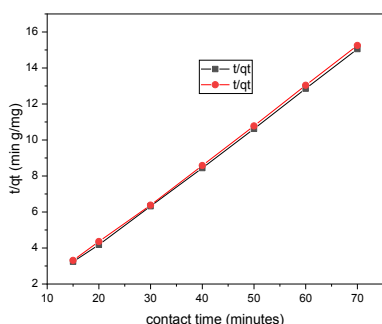


Fig.10: Pseudo-second order for adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> onto amc Fig.11: Boyd Kinetic model plot for adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> onto amc

Power function and Elovich model do not provide good fit for adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> onto activated maize cob as can be seen by poor R<sup>2</sup> values. The Power function constants **a** and **b**; the Elovich constants **α** and **β** as well as their R<sup>2</sup> values are shown in table 4 (figures not shown). The intra-particle diffusion model was used in explaining the adsorption mechanism. The non-linearity of the Weber Morris plots (not shown) for the adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> onto activated maize cob suggested that intra-particle diffusion was not the only rate limiting step, and that some other mechanism along with intra-particle diffusion is involved. The Weber Morris constant k<sub>id</sub> and C are given in table 4.

Boyd kinetic model was used to determine the actual rate controlling step involved in this study. Because the Boyd kinetic model plot (Fig.11) is neither linear nor passes through the origin, film diffusion is the rate limiting step involved for the adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> onto activated maize cob (Mohan and Singh 2002). Boyd kinetic model constants B, C and R<sup>2</sup> of the plot are shown in table 4.

Table 3: Pseudo-first and second order kinetic model parameters for Cu<sup>2+</sup> and Pb<sup>2+</sup> adsorption onto a mc

Pseudo-first order model				Pseudo-second order model			
q <sub>e</sub> (exp) (mg/g)	k <sub>1</sub> (min <sup>-1</sup> )	q <sub>e</sub> (cal) (mg/g)	R <sup>2</sup>	h (mg/g/min)	k <sub>2</sub> (g/mg/min)	q <sub>e</sub> (cal) (mg/g)	R <sup>2</sup>
Pb <sup>2+</sup>							
4.79	0.02280	0.0248	0.235	9.497	0.441	4.64	0.999
Cu <sup>2+</sup>							
4.71	0.003915	0.0615	0.007	25.707	1.215	4.60	0.999

Table 4: Elovich, Power function, Intra-particle and Boyd kinetic model parameters for Cu<sup>2+</sup> and Pb<sup>2+</sup> adsorption onto amc

Elovich	α(mg/g/min)	β(mg/g/min)	R <sup>2</sup>
Pb <sup>2+</sup>	0	-55.56	0.034
Cu <sup>2+</sup>	3.683x10 <sup>61</sup>	32.26	0.105
Power function	A	B	R <sup>2</sup>
Pb <sup>2+</sup>	4.78	-0.004	0.050
Cu <sup>2+</sup>	4.50	0.007	0.122
Intra-particle diffusion	k <sub>id</sub> (mg/g/min <sup>0.5</sup> )	C (mg/g)	R <sup>2</sup>
Pb <sup>2+</sup>	-0.009	4.760	0.073
Cu <sup>2+</sup>	0.007	4.568	0.053
Boyd model	B (min <sup>-1</sup> )	C	R <sup>2</sup>
Pb <sup>2+</sup>	-0.023	4.789	0.235
Cu <sup>2+</sup>	-0.004	3.864	0.007

### ADSORPTION ISOTHERM STUDIES

Table 5: Isotherm model parameters for the adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions onto amc.

Isotherm	Parameters		
<b>Langmuir</b>	$q_{max}$ (mg/g)	$K_L$ (Lg <sup>-1</sup> )	$R^2$
Pb <sup>2+</sup>	12.5	0.180	0.952
Cu <sup>2+</sup>	14.5	0.094	0.970
<b>Freundlich</b>	$K_f$ (mg/g)(L/mg) <sup>1/n</sup>	$n$	$R^2$
Pb <sup>2+</sup>	2.936	2.583	0.988
Cu <sup>2+</sup>	1.850	1.875	0.999
<b>Harkins and Jura</b>	<b>A</b>	<b>B</b>	$R^2$
Pb <sup>2+</sup>	10.616	1.349	0.931
Cu <sup>2+</sup>	7.692	1.350	0.867
<b>Halsey</b>	$n_H$	$K_H$	$R^2$
Pb <sup>2+</sup>	2.613	0.059	0.987
Cu <sup>2+</sup>	1.880	0.308	0.999
<b>Temkin</b>	$B$ (kJ/mol)	$K_T$ (L/g)	$R^2$
Pb <sup>2+</sup>	2.105	3.981	0.907
Cu <sup>2+</sup>	2.966	1.111	0.960
<b>D-R</b>	$q_m$ (mg/g)	$E$ (kJ/mol)	$R^2$
Pb <sup>2+</sup>	7.765	1.678	0.745
Cu <sup>2+</sup>	8.070	0.742	0.806

The Langmuir plots (Fig 12) are linear with a reasonably high linear regression coefficient  $R^2$  values (table 5) suggesting that the adsorption process obeys the Langmuir model. In addition, the  $R_L$  values of Cu<sup>2+</sup> and Pb<sup>2+</sup> adsorption onto the adsorbent are between 0 and 1, showing that the Langmuir isotherm is favourable.

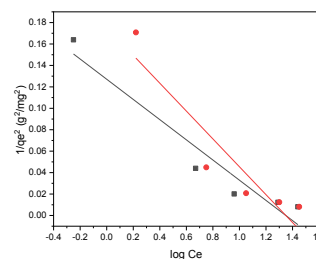
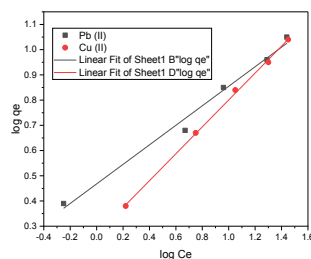
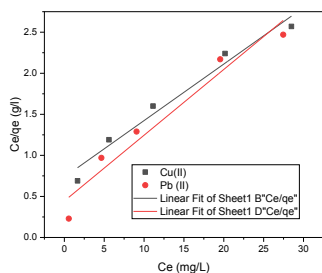


Fig 12: Langmuir adsorption isotherm of Pb<sup>2+</sup> and Cu<sup>2+</sup> onto amc Fig 13: Freundlich isotherm plot of adsorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> onto amc Fig 14: Harkins and Jura isotherm plot of adsorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> onto amc

### FREUNDLICH ISOTHERM

The  $K_f$  values and the adsorption intensities  $n$  (table 5) obtained from the Freundlich model plots (Fig 13) suggest that the metal binding affinity of Pb<sup>2+</sup> onto activated maize cob is higher than of Cu<sup>2+</sup>. The higher value of  $K_f$  indicates higher adsorption capacity for metal ions and the values of  $n$  lies between 1-10 indicating favorable adsorption (Lakatos *et al.*, 2002; Mohamed *et al.*, 2012). The linear regression coefficients  $R^2$  of the experimental data show that the adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions onto the adsorbent fitted well to the Freundlich isotherm model.

### HARKINS AND JURA ISOTHERM

The summary of Harkins and Jura isotherm model parameters obtained from the Harkins and Jura isotherm plots (Fig 14) is shown in table 5. The correlation coefficient value  $R^2$  of Pb<sup>2+</sup> adsorption is higher than that of Cu<sup>2+</sup>. This shows that adsorption of Pb<sup>2+</sup> onto the adsorbents fit better for this isotherm than Cu<sup>2+</sup>.

### HALSEY ISOTHERM

From table 5, it can be seen that the correlation coefficient values  $R^2$  for adsorption of Cu<sup>2+</sup>

and  $Pb^{2+}$  ions onto activated maize cob are both high. This shows that adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  fits Halsey isotherm model. The fitting of the experimental data to Halsey isotherm equation attest to the heteroporous nature of the adsorbents (Halsey, 1948).

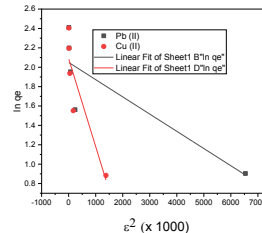
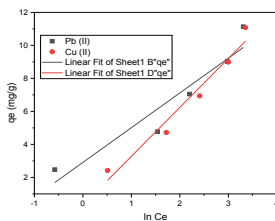
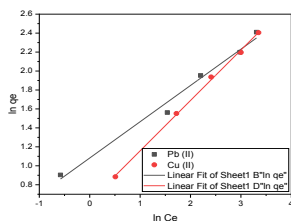


Fig 15: Halsey isotherm plot    Fig 16: Temkin isotherm plot of adsorption    Fig 17: D-R isotherm plot of adsorption of  $Pb^{2+}$  and  $Cu^{2+}$  onto amc

### TEMKIN ISOTHERM

Assessment of the values of correlation coefficient  $R^2$  of Temkin isotherm plot (Fig 16) showed that Temkin model is another good model for the description of the adsorption of the metal ions by the adsorbent. Their values are all high but lower than those of Langmuir, Freundlich, Harkins and Jura and Halsey isotherm models.

### DUBININ-RADUSHKEVICH (D-R) ISOTHERM

The non-linearity of D-R plot (Fig 17) showed that D-R isotherm is not a good model for the description of action of  $Pb^{2+}$  and  $Cu^{2+}$  onto amc. From table 5, it can be observed that the values of mean D-R energy  $E$  are below  $8\text{kJ/mol}$  indicating physical adsorption. However, the value of correlation coefficient  $R^2$  are low suggesting that physisorption may not have played a dominant role in the adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  ions onto activated maize cob.

### CONCLUSION

In this study, adsorption process for the removal of  $Cu^{2+}$  and  $Pb^{2+}$  from aqueous solution by using activated maize cob has been presented. For the different operational parameters, maximum adsorption of  $Pb^{2+}$  was 20 minutes at  $20^\circ\text{C}$  while that of  $Cu^{2+}$  was 30 minutes at  $60^\circ\text{C}$ . Kinetics of adsorption process of  $Cu^{2+}$  and  $Pb^{2+}$  by the adsorbent is best described by pseudo-second order rate model whereas their mechanism is film diffusion. Adsorption of both metal ions onto amc is feasible since the values of  $\Delta G$  are negative at various temperatures;  $Cu^{2+}$  is endothermic with  $\Delta H$  being positive while  $Pb^{2+}$  is exothermic with negative  $\Delta H$  value. Isotherm studies revealed that the correlation coefficient  $R^2$  values are all high and the fitting of this adsorption process is in order of Freundlich > Halsey > Langmuir > Temkin > Harkins and Jura > Dubinin-Radushkevich isotherms. Morphological investigation showed that activated maize cob has active pores and ionisable functional groups at the surface which enhance its adsorption capacity. As a result of this study, it may be concluded that locally available maize cob can be activated and used as sorbent for heavy metals removal, representing an effective and environmentally clean utilization of waste matter.

### REFERENCES

1. Ajmal M.; Rao, R.A.K.; Anwar, J.A. and Ahmad R. (2003): Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater. *Bioresources Technology*, 86: 147-149.
2. Aksu Z. (2002): Determination of the equilibrium, kinetics and thermodynamic parameters of the batch biosorption of lead (ii) ions onto chlorella vulgaris. *Process Biochemistry* 38, 89-99.

3. Aksu Z. and Kutsal T. (1991): A bioseparation process for removing Pb<sup>2+</sup> ion from waste water by using *C. vulgaris*. *Journal of Chemical Technology and Biotechnology*. 52,109-118.
4. Ali H, Khan E, and Sajad M.A. (2013): Phytoremediation of heavy metals—Concepts and applications. *Chemosphere* 91, 869-881.
5. Argun M A, Dursun S., Ozdemir C and Karatas M (2007): *Journal of Hazardous materials*. 141, 77-85.
6. Aydin, H.; Bulut Y. and Yerlikaya C. (2008): Removal of Cu (ii) ion from aqueous solutions by adsorption onto low cost adsorbent. *Journal of Environmental Management*, 87:37-45.
7. Bazar C A (2006): Applicability of the various adsorption models of three dyes adsorbed onto activated carbon prepared from waste apricot. *Journal of Hazardous Materials*. B134,232-241
8. Boyd G E, Adamson A W and Myers Jr L S (1947): The exchange adsorption of ions from aqueous solutions by organic zeolite II: kinetics, *Journal of American Chemical Society* 69, 2836-2848.
9. Chingombe P, Saha B and Wakeman R J (2006): Sorption of atrazine on conventional and surface modified activated carbons. *Journal of colloid and interface science* 302,408-416.
10. Chowdhury Z Z, Zain S M, Khan R A and Ahmed A A (2010): Equilibrium, Kinetics and Isotherm studies of Cu(ii) adsorption from waste water onto alkali activated oil palm ash. *American Journal of Applied science* 8(3): 230-237.
11. Chowdhury Z Z, Zain S M, Khan R A and Khalid K (2011): Linear regression analysis for the kinetics and isotherm studies of sorption of manganese (ii) ions onto activated palm ash from waste water. *Oriental Journal of Chemistry*. Vol. 27(2):405-415.
12. Crini G. (2006): Non conventional low cost adsorbents for heavy metal removal: a review. *Journal of Bioresources Technology* 97: 1062-1070.
13. Elsayed A E, Mahdy A M and Bbrakat N H (2007): Thermodynamics of copper desorption from soils as affected by citrate and succinate. *Soil and water Resources Journal* 2(4):135-140.
14. Gadd G.M. (2001): Accumulation and transformation of metals by microorganisms., in: Rehm H. J., Reed G., Puhler A., and Stadler, P. (Ed.), *Biotechnology, a Multivolume Comprehensive Treatise, Special Processes*, Wiley-VCH, Weinheim. 225-264.
15. Halsey J. (1948): *Journal of chemical Physics*. 16, 931
16. Han R P, Zhang J H, Zou W H, Shi J and Liu H M (2005): Equilibrium biosorption isotherm for lead ion on Chaff. *Journal of Hazardous Materials*. B,125,266-271.
17. Han R, Lu Z, Zou W, Daotong W, Shi J and JiuJun Y. (2006): Removal of copper (ii) and lead (ii) from aqueous solution by manganese oxide coated sand: ii. Equilibrium study and competitive adsorption. *Journal of Hazardous materials* 137: 480-488.
18. Harkins W D and Jura C J. (1944): The Decrease of free surface energy as a basis for the development of equations for adsorption isotherms; and the existence of two condensed phases in films on solids. *Journal of Chemical Physics* 12, 112-113.
19. Ho Y S and McKay G (1999): Pseudo-second order model for sorption process. *Process Biochemistry* 34: 451-465.
20. Ho, Y. S. (2003): Removal of copper ions from aqueous solution by tree fern. *Water Resources* 37, 2323-2330
21. Isah A L. (2010): Death toll in Zamfara Lead poisoning hits 300. *The Guardian* Jun 6, p 1-2.
22. Kim T I, Pask S K, Cho S Y, Kim H B, Kang Y, Kim S D and Kim S J (2005): Adsorption of heavy metals by brewery biomass. *Korean Journal Chemical Engineering* 22(1):91-98

23. Krishnani K K, Parmala V and Meng X (2004): Detoxification of chromium (vi) in coastal waste using lignocellulosic agricultural waste. *Water SA* 30(4): 541- 545.
24. Kumar K V and Porkodi K (2007): mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using paspalum notatum. *Journal Hazardous materials* 146(1), 214-226.
25. Lakatos J, Brown S D and Snape C E (2002): Coals as sorbent for the removal and reduction of hexavalent chromium from aqueous waste streams. *Fuels* 81,691-698.
26. Lisa N, Kanagaratnam B and Trever M (2004): Biosorption of Zinc from aqueous solutions using biosolids. *Advanced Environmental Resources*, 8.629-635.
27. Malakul P., Srinivasan K.P. and Wang, H.Y. (2002). Metal adsorption and desorption characteristics of surfactant- modified clay complexes. *Industrial Engineering and Chemical Resources* 37:4296-4301
28. Malkoc C and Nuhoghi Y (2005): Investigations of Ni (ii) removal from aqueous solutions using tea factory waste. *Journal of Hazardous materials*.127, 120-128
29. Mataka L.M., Henry E.M.T., Masamba W.R.L., and Sajidu S.M. (2006): Lead remediation of contaminated water using Moringa Stenopetala and Moringa oleifera seed powder. *International Journal of Environmental Science & Technology* 3, 131-139.
30. Mohamed M A, Wanees S A, Ahmed A M M and Adam M S (2012): Adsorption studies on the removal of hexavalent chromium contaminated waste water using activated carbon and bentonite. *Chemistry Journal*, 2 (3), 95-105
31. Mohan D and Singh K P (2002): Single and multi-component adsorption of cadmium and zinc using carbon derived from bargasse- an agricultural waste. *Water research* 36, 2304-2318..
32. Okuo J.M. and Ozioko A.C. (2001): Adsorption of Lead and Mercury ions on chemically treated periwinkle shells. *Journal chemistry Society of Nigeria* 26(1), 60-65.
33. Pandey K K, Prasad G and Singh V N (1986): Use of wollastonite for the treatment of Cu (II) rich effluent. *Water, air and soil pollution* 27, 287-296.
34. Rounak-Shariff M, and Kafia-Shareef M (2011): Thermodynamic adsorption of Herbicides on eight agricultural soils. *International Journal of Scientific and Engineering Research*. 2(6):238-245.
35. Sadeeq A G (2010): Zamfara releases 240 million naira over mining death. Daily Trust, Jun 7, p 2.
36. Sag Y and Kutsal T. (2000): Determination of the biosorption heats of heavy metal ions on zoogloea ramigera and rhizopus arrhizus. *Biochemical Engineering Journal* 6,145-151.
37. Singh K.K.R. and Hasan S.H. (2005): Removal of cadmium from wastewater using agricultural waste 'rice polish'. *Journal of Hazardous Materials* a121, 51-58.
38. Singha B and Das S K (2013): *colloids and surfaces*. B(107),97-106.
39. Siti N A A, Mohd H S I, Md L K and Shamsul I. (2013): adsorption process of heavy metals by low-cost adsorbent: a review. *World Applied Science Journal* 28(11), 1518-1530.
40. Sparks D L (1986): Kinetics of reaction in pure and mixed systems in the soil physical chemistry. Boca Raton CRC press. 12-18.
41. Temkin M I and Pyzhev V. (1940): kinetics of ammonia synthesis on promoted iron catalyst. *Acta Phys. Chim. USSR* 12, 327-356.
42. Upendra K. (2006): Agricultural products and by-products as low cost adsorbent for heavy metal removal from water and waste water : A review. *Scientific Research and Essay* 1, (2): 33-37.

43. Vadivelan V and Kumar K V. (2005): Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk. *Journal of colloid and interface science* 286, 90-100.
44. Venkata M S, Ramanaiah S V and Sarma P N. (2008): Biosorption of direct azo dye from aqueous phase onto spirogyra sp. 102: Evaluation of kinetics and mechanistic aspects. *Biochemical Engineering Journal* 38(1), 61-69.
45. Weber W J and Morris J C. (1963): Kinetics of adsorption on carbon from solution. *J. sanit. Eng. Div.Am.Soc. Civ. Eng.* 89(1):31-60
46. Xiao F and Ju-Chang HH (2009): Comparison of biosorbents with organic sorbents for removing Copper (II) from aqueous solutions. *Journal of Environmental Man.,* 90: 3105-3109.