EVALUATION OF ACTIVATED CARBON FROM MAIZE COBS AS LOW-COST ADSORBENT FOR ADSORPTION OF PB (II) IONS FROM AQUEOUS SOLUTION OF THE SALT

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ABSTRACT

Heavy metal adsorption technology by biomass has some major advantages in reducing the concentration of heavy metal ions to very low levels. A carbonaceous adsorbent was prepared from maize cobs by acid treatment and was tested for its efficiency in removing Lead (II). Effect of initial lead concentration, contact time and pH of solution were also investigated. The Kinetic data were analyzed using various Kinetic models. Particularly Pseudo - First order, Pseudo - Second order, Intraparticle diffusion and correlations. Result shows that the Pseudo – Second order Kinetic model was found to agree with the experimental data. Equilibrium isotherm data tested using two models – Langmuir and Freundlich. Equilibrium data agree well with Langmuir model. The maximum adsorption capacity of Lead by Activated Carbon from maize cob determined from Langmuir model was 3.15mg/g at pH 5. Adsorption equilibrium was established in about 90 min.

Key words: Adsorption, Kinetic, Langmuir isotherm, Lead ion, Adsorbent

INTRODUCTION

The tremendous increase in the amount of Lead in aquatic environment has become a major concern by scientists all over the world. Lead is one of the toxic heavy metals widely discharged into the environment as industrial waste in many countries, causing serious soil and water pollution. Lead has been known to pollute the environment by waste streams, which originates from metallurgical industry, electroplating and metal finishing industries, Petroleum refining and drainage from ore mines. According to Bhattacharyya and Gupta (2006), Lead can enter or adsorbed into human body through inhalation, skin contact, or with diet, resulting in adverse health effects on every system in the body. Excessive exposure to lead may lead to anemia, mental retardation, coma, seizures and bizarre behavior (Botkin and Keller, 2000). The world economic today is focusing on better waste management policies; hence the need to reduced wastes is to protect the environment (EU, 2010).

Numerous methods have been introduced for removing Lead from waste waters mainly chemical, precipitation, chemical oxidation or reduction, ultra filtration, electrochemical treatment, reverse osmosis, phytoextraction, electrolydiayses, application of membrane technology, evaporation recovery, solvent extraction and ion exchange processes.

However, the aforementioned techniques are very expensive, may produce large volume of wastes and not economically

feasible for small and medium industries (Aksu, 2005; Volesky, 1990).

Adsorption process using natural adsorbent or agricultural waste products are becoming the new alternative for waste water treatment because they are cheap, simple, sludge free and involve small initial cost and land investment. Heavy metals adsorption technology by biomass has some major advantages especially its effectiveness in reducing the concentration of heavy metal ions to very low levels and the adsorbent materials itself are expensive (Volesky, 1994).

In this work, the effectiveness of adsorption of Lead (II) ions by activated carbon from Maize Cobs has been ranked one of the important crops in the world (Ekanem, 1996). It is also a versatile crop grown across a range of agro – ecological zones. The grains, leaves, tassels and cobs can all be used to produce a large variety of food and non-food products giving the maize plant its high economic value (IITA, 2009). This study determines the parameters that influence adsorption of Lead such as pH of the solution, initial lead concentration and contact time. The Kinetic Models and Equilibrium isotherm were also studied.

MATERIALS AND METHOD

Preparation of Adsorbent

In the present study, maize cobs were used for the preparation of activated carbon. The maize cobs were collected from the Kaduna Agricultural Development Projection (KADP) Samaru Kataf Farm and cleaned to remove loose flakes. The raw material was washed several times using tap water and finally distilled water. It was subsequently air-dried to remove excess water content. The dried samples were crushed using pestle and motar into fine particles sizes. The samples were then stored in a clean polythene bag until analysis.

The maize cob was carbonised at 500°C for 40min according to method as described by Gimba and Bahago (2004).

Briefly a portion (2g) of the maize cob was weighed into crucible and mixed thoroughly with 2cm^3 each of 0.10M H_3PO_4 at optimum conditions of temperature and time in a muffle furnace model GLM 3+ DL/IND for activation. The activated carbon was then washed with deionised water and soaked in 1% $NaHCO_3$ solution to remove any remaining acid. The samples were further washed with deionised water until no acidity and then dried at 105°C for 5 hours (Dermibas *et al*., 2004). The dried material was grounded and sieved to obtain the particle sizes of 300 - 850µm (Kagbu, 2001; Pattabhi *et al*., 2008) and stored in airtight container for further experiments.

Fourier Transform Infrared Spectrophotometer (FT – IR) Analysis.

The activated carbon product was characterized for its functional group using **FTIR spectrometer** (**Nicolet Magna-IR Model 550**) analysis. For this, the activated carbon samples were brought to the constant weight in a drying oven at 50°c for 24h and kept in the desiccators. Exactly 1mg dried activated carbon was mixed with 100mg KBr, which was initially dried at 110°c in the sample disk. The FT – IR spectra was in the range of 450 – 400cm^{-I}. The absorption spectra were collected and analysed (Patnukao *et al*., 2008).

Preparation of Adsorbate

Pb (II) stock, solution (1000mg/L) was prepared in deionised water using analytical grade Lead nitrate ($Pb(NO_3)_2$). The working solution was obtained by diluting the stock solution in deionised water.

Batch Mode Adsorption Studies

Adsorption studies were performed in 100ml flasks where solutions of Pb ions

(25ml) with different initial concentrations (5 – 20mg/L). Equal mass of 0.2g of maize cob of approximate a particle size of 355µm was added to each metal ion solution and each sample was kept in shaker for 180 min at room temperature of 30°c (Ahmed and Kumar, 2008) to reach equilibrium. The flasks were then removed from shaker and final concentration of chromium ion in the solution was analysed by using UNICAM 968 Atomic Absorption Spectrophotometer at 540nm. The adsorption capacity at equilibrium qe (mg/g) was calculated by

$$qe = (Ci - Ce)V/M \quad \text{.....}$$

where Ci and Ce (mg/L) are the liquid phase concentrations of chromium ion at initial and equilibrium concentrations respectively. V is the volume of the solution (L) and M is the mass dry adsorbent used (g). The effect of initial contact time, and pH were studied. Adsorption Kinetic and Adsorption isotherm were applied to equilibrium data.

RESULTS AND DISCUSSION

FTIR Spectrum

The Table 1 demonstrates that, after the adsorption the shifting occurs both to higher and lower wave numbers. This shift indicated that there were binding processes taking place on the surface of activated carbon (Pevasant *et al.*, 2003). The functional groups involved in the adsorption were as follows: Broad band 3750.26 – 3455.76cm^{-1} representing bonded OH groups and NH groups (Stuart, 2004) 2921.37 – 1952.67cm^{-1}, the aliphatic C-H groups, 1952.67-1561.07cm^{-1} , the C = O stretching group and 1037.01cm^{-1}, P-O-C stretching in a chain. These functional groups could act as chemical binding agents where carboxyl, hydroxyl and amine groups could dissociate negatively charged active surface. This means that these functional groups could attract the positively charge objects such as heavy metal ions (Volesky, 1990)

Table 1: Fourier Transform Infrared Spectrophotometer (FT-IR) Analysis of Activated Carbon prepared from Maize Cobs

FTIR Peak	Original Adsorption	Pb(II) Loaded Ac Diff	Assignment
1.	3750.26	3745.10 +5.16	Bonded-OH
2.	3455.76	3417.16 +38.60	Bonded-NH
3.	2921.37	2914.50 -6.87	Aliphatic C-H group
4.	1952.67	1957.60 - 4.93	Aliphatic C-H group for anhydride C=O stretching
5.	1561.07	1452.51 +8.56	C=O stretching
6.	1037.01	1037.67 -0.66	P-O-C stretching

Table 2 was deduced by plotting log (qe – qt) against (t) as shown in Figure 1 for Pb(II) ions adsorption on MCA with Ci = 5, 10, 15 and 20mg/1 at 30°C. The qeexp and qecal values were values were found to be far from each other. Experimental results did not follow first order kinetics given by equation (4) as there was difference in two important aspects: (1) K_f (qe - qt) does not represent the number of available sites, and (ii) log qe was not equal to the intercept of the plot of log (qe – qt) Vs t.

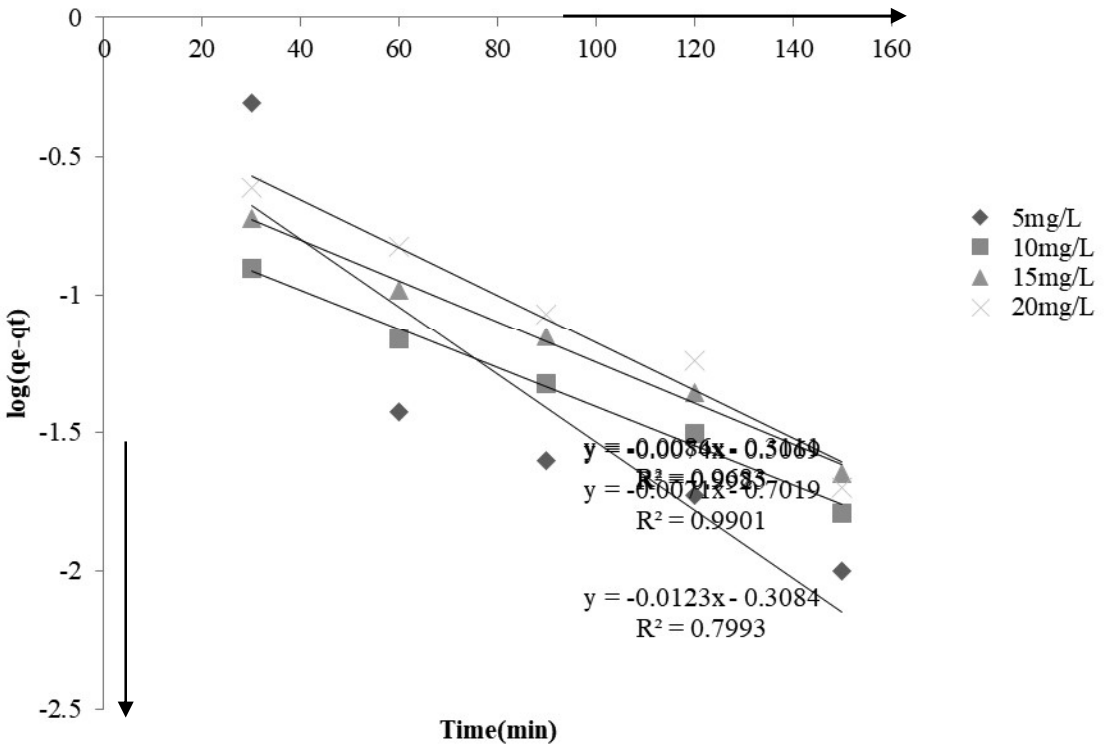

Figure 1: Lagergren plots for Pb (II) ions Adsorption in Aqueous Solutions.

Table 2: Kinetic Parameters For The Removal of Pb(II) ionsBy MCA (T = 303K, M= 0.2g/L)Pseudo First – Order Model

Ci(mg/ L)	qe, exp(mg/g)	qe, cal(mg/g)	$K_f(min^{-1})$	R^2
5	0.5375	0.4916	0.02833	0.7993
10	1.0625	0.1987	0.01635	0.9901
15	1.5888	0.3112	0.01700	0.9925
20	2.1000	0.4885	0.01981	0.9683

Table 3 was deduced by plotting t/qt against t (Fig. 2), and h is obtained from intercept. Since qe is known from the slope,
Ks can be determined from the value of h. Tables 3, the qeexp and the qecal values from the pseudo – second – order kinetic model are very close to each other. The calculated correlation coefficients are also closer to unity for the pseudo – second – order kinetic than for the pseudo – first order kinetic model. Therefore, the adsorption can be approximated more appropriately by the pseudo – second – order kinetic model for the adsorption of Pb(II) onto MCA. Mathialagan and Viraraghavan (2002) and Taly – Costodes *et al* (2003) have reported Ks values of 0.061 and 0.305 g/mg/min for Cd(II) adsorption on perlite and saw dust of PinusSylerstris, respectively. Ks values in the range of 0.0083 – 0.0215 g/mg min have been reported by Padmavathy *et al*

(2003) for the adsorption of Ni(II) onto baker'syeast.

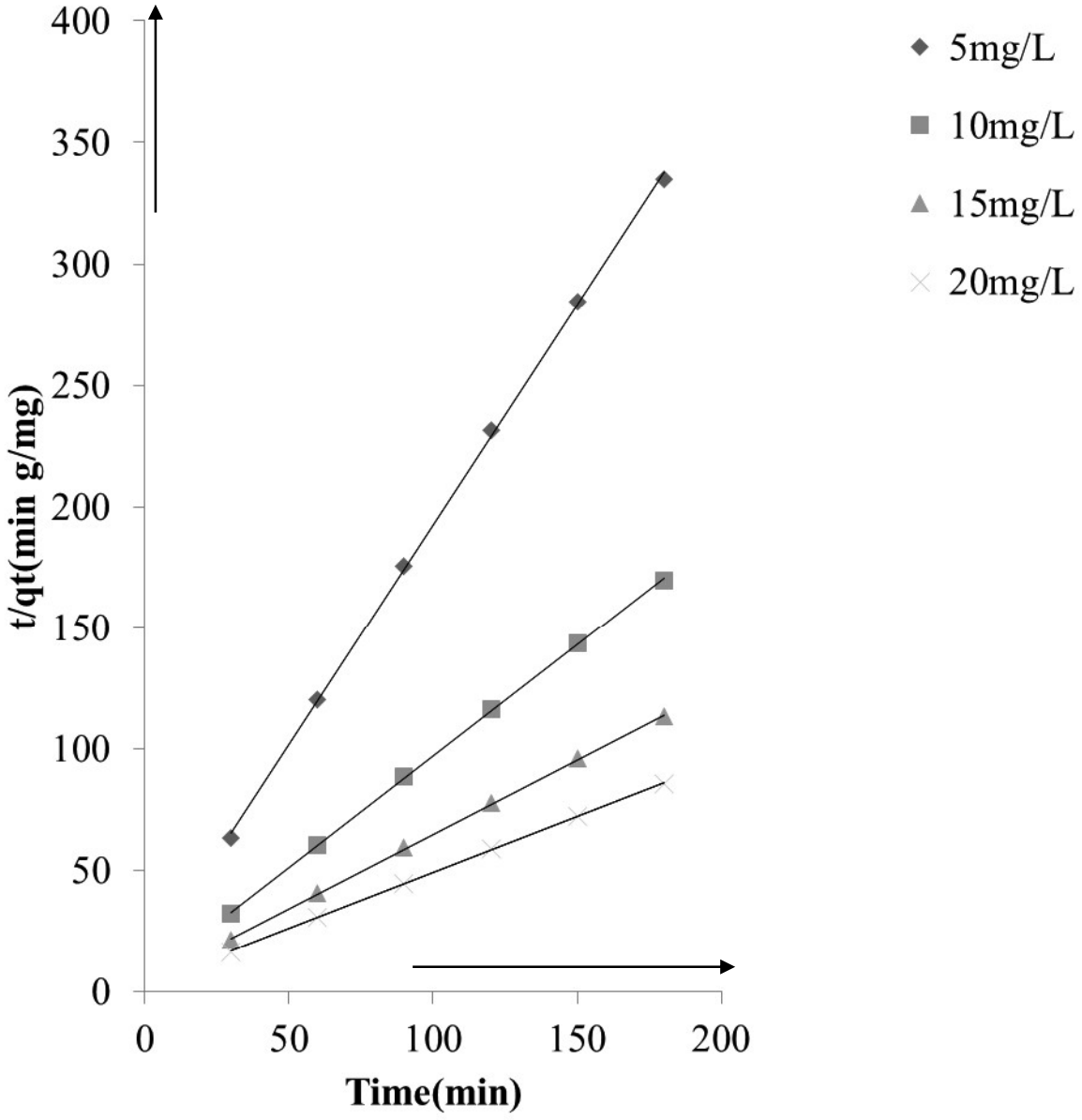

Figure 2: Pseudo- second order kinetic plot for the removal of Pb(II) ions by MCA

Table 3: Pseudo Second – Order Model for Pb(II) ions

Ci(mg/l)	qe, exp (mg/g)	qe, cal (mg/g)	h (mg/g min)	Ks (g/mg min)	R^2
5	0.5375	0.5505	0.0925	0.3053	0.9996
10	1.0625	1.0896	0.1877	0.1581	0.9997
15	1.5888	1.6308	0.2787	0.1048	0.9998
20	2.1000	2.1612	0.3596	0.0769	0.9998

Table 4 was deduced by plotting qt against $t^{0.5}$. The extrapolation of the linear portions of the plots back to the y – axis gives intercept which provide the boundary of layer thickness. The slope of the Weber and Morris plots is defined as the parameter, characteristic of the rate values of kid is found higher in Pb(II). This shows that Weber and Morris model shows better representation than pseudo – first order kinetic model.

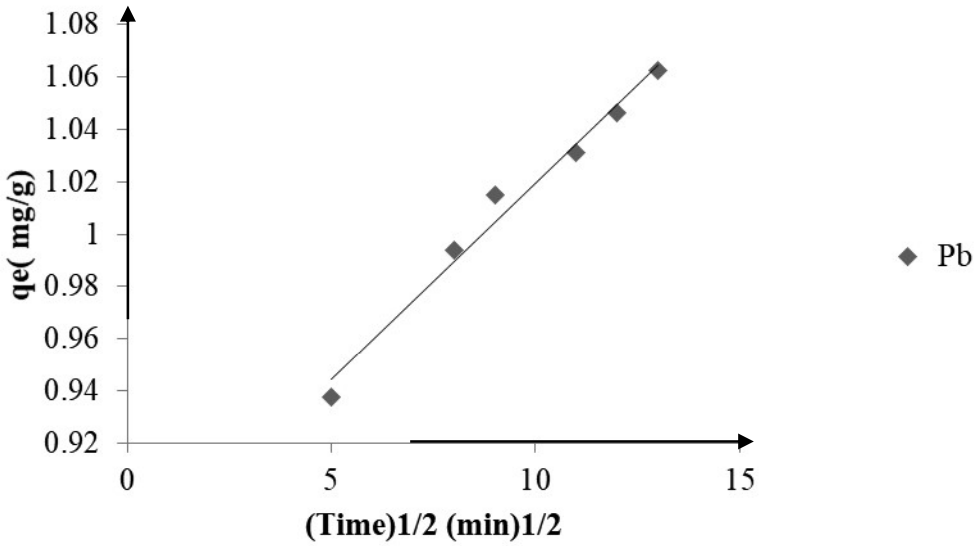

Fig. 3: Weber and Morris intraparticle diffusion plot for the removal of Pb(II) ions by MCA (T=303K, Ci=20mg/L ,m=0.2mg/L).

Table 4: Weber And Morris Intra-Particle Diffusion for The Removal of Pb(II) ions, and Cr (VI) ions by MCA (T = 303K, Ci = 10mg/L, M = 0.2g/L)

Pb(II) ions

Kid(mg/g min	0.0150
I (mg/g)	0.8694
R^2	0.9797

Table 5 was deduced by plotting log R against log t. The correlations of the values of log R(% removal) and log (time) (Fig. 3) also resulted in linear relationship, as evidenced by R^2 – values close to unity (Table4).

This also indicates that the process of intra-particle diffusion is taking place in these adsorption systems. The divergence in the value of slope from 0.5 indicates the presence of intra-particle diffusion process as one of the rate limiting steps (McKay, *et al.*,1980)

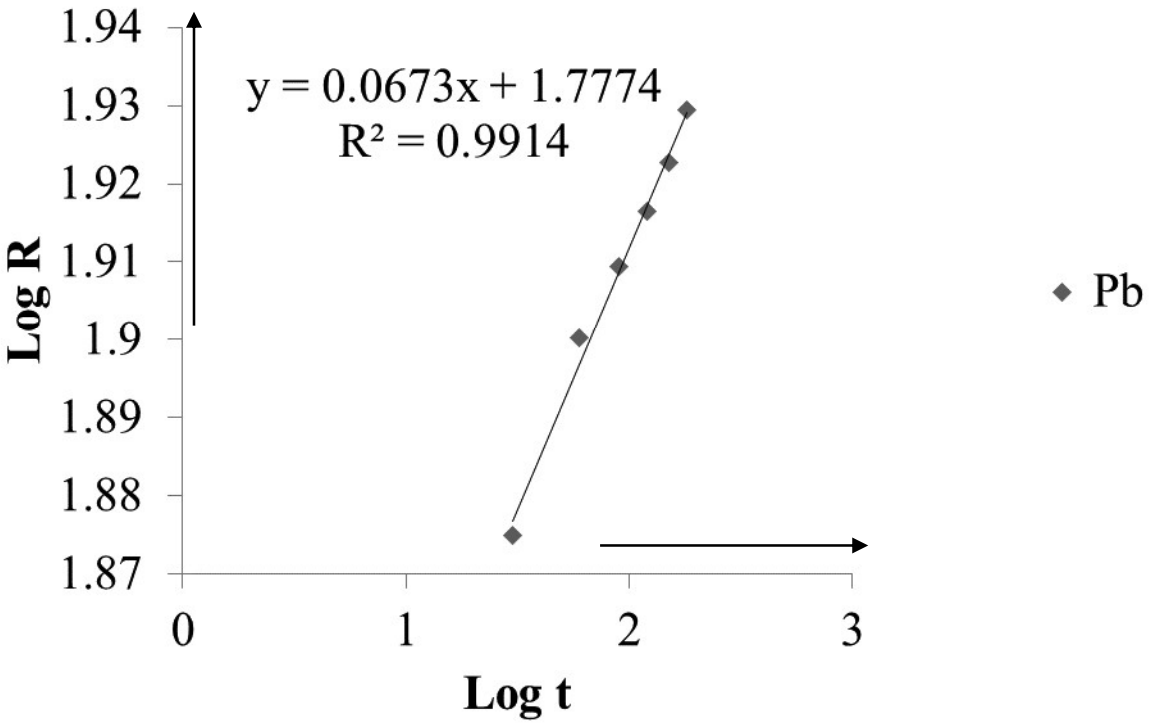

Fig. 4: The correlation of the values of Log(R%) and Log(time) for the Pb(II)and Cr (VI) ions.

Table 5: The Correlation of the Values of Log (% Removal) And Log (Time) For The Various Metal Ions

	Pb(II) ions
Slope	0.0673
Intercept	0.2498
R^2	0.9914

Adsorption Isotherms

Table 6 was deduced by plotting Ce/qe against Ce. The values of Langmuir and Freundlich constants were obtained.

(Fig. 5) indicates that the adsorption of adsorbate on activated carbon follows the Langmuir isotherm. The Langmuir constant value is given in Table 6. The maximum adsorption capacity Qo, showed that the maize cob had a mass capacity for Pb^{2+} (3.150mg/g). The b is related to the apparent energy of adsorption for Pb^{2+} (0.5453L/mg). This showed that the energy of adsorption is not favourable to Pb^{2+} probably due to its large ionic radius; hence all binding sites may not be available to Pb^{2+}. This preferential adsorption could be explained in terms of ionic radius of the metal ion. Adsorption of the metal was tested using separation factor R_L.

The separation parameter for the metal is less than unity indicating that maize cob biomass is an excellent adsorbent.

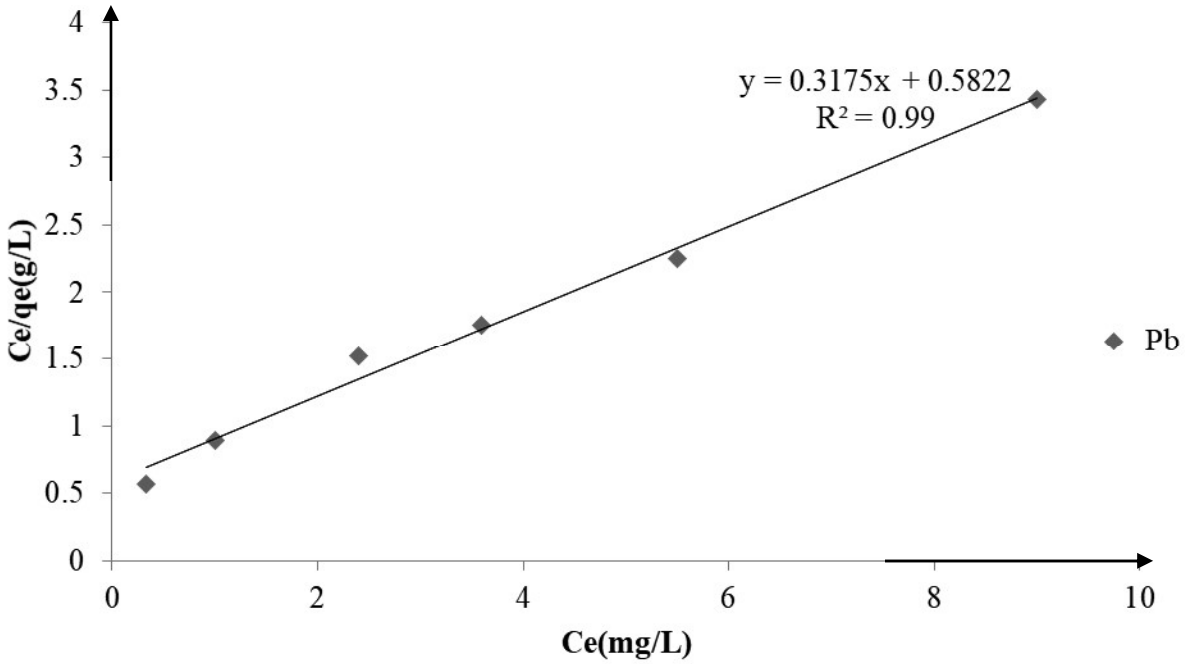

Fig. 5: Langmuir isotherm plot for Pb(II) ions adsorption in aqueous solutions

Table 6: Sorption Isotherm Constants Coefficients of Activated Carbon prepared from Maize Cobs.

Adsorbate	**Langmuir Constant**				**Freundlich Constant**		
	Q max (mg/g)	**b(L/mg)**	**R^2**	**R_L**	**K_F(mg/g)**	**N**	**R^2**
Lead	3.1500	0.5453	0.9900	0.0576	1.0488	2.1368	0.9818

Fig. 6 reveals the plots of log qe against log Ce. The linear logarithmic plots show that the adsorption followed Freundlich model It also indicates that the average energy of adsorption decreases with increasing adsorption capacity values of K_F and n were calculated from the intercept and slope and are given in Table 6 along with the Langmuir constants. The value of n between 1 and 10 represent good adsorption of the adsorbate onto the adsorbent (McKay et al., 1982). Values of Qe predicted by both models, as wells as the experimental values, are in Fig. 6 for Lead and Chromium ions. They also show that the Langmuir model fitted the results slightly better than Freundlich model.

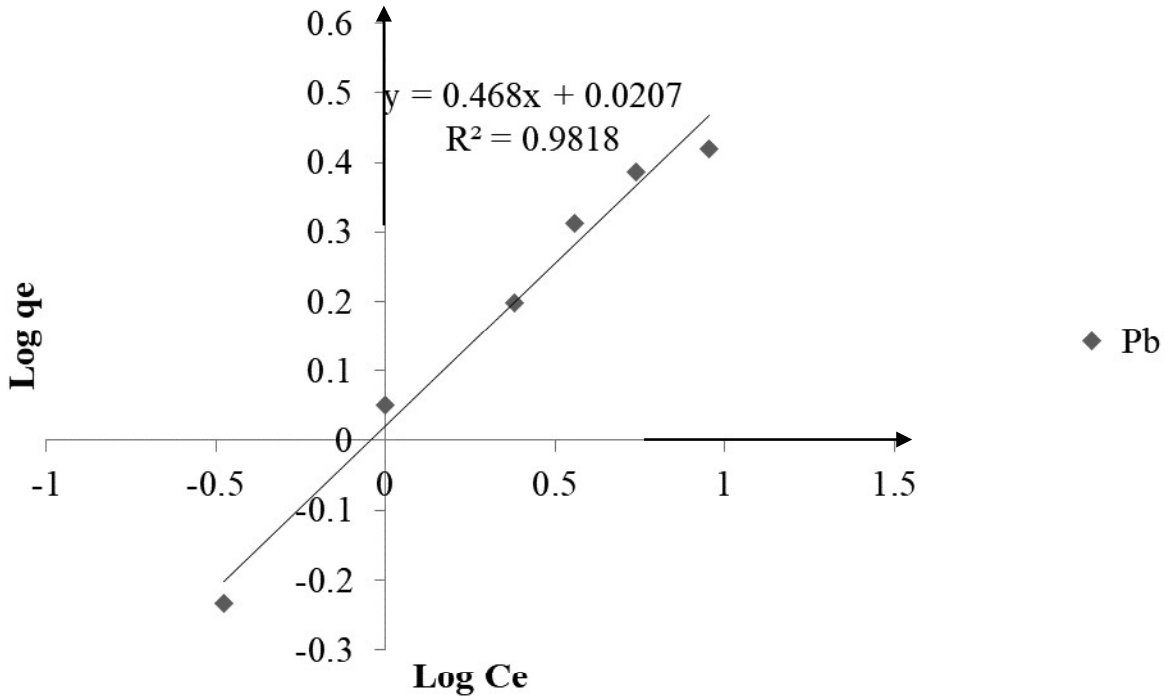

Fig. 6: Freundlich isotherm plot for Pb(II) ions adsorption in aqueous solutions

Effect of Contact Time

Fig. 7 reveals that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The adsorption capacity of Lead metal increased rapidly in the beginning of the reaction and reached equilibrium at 90min. A shortage contact time necessary to reach equilibrium indicates that the predominant mechanism is chemisorptions. The contact time obtained in this study indicates that chemisorptions may be involved (Ho *et al*.,1996).

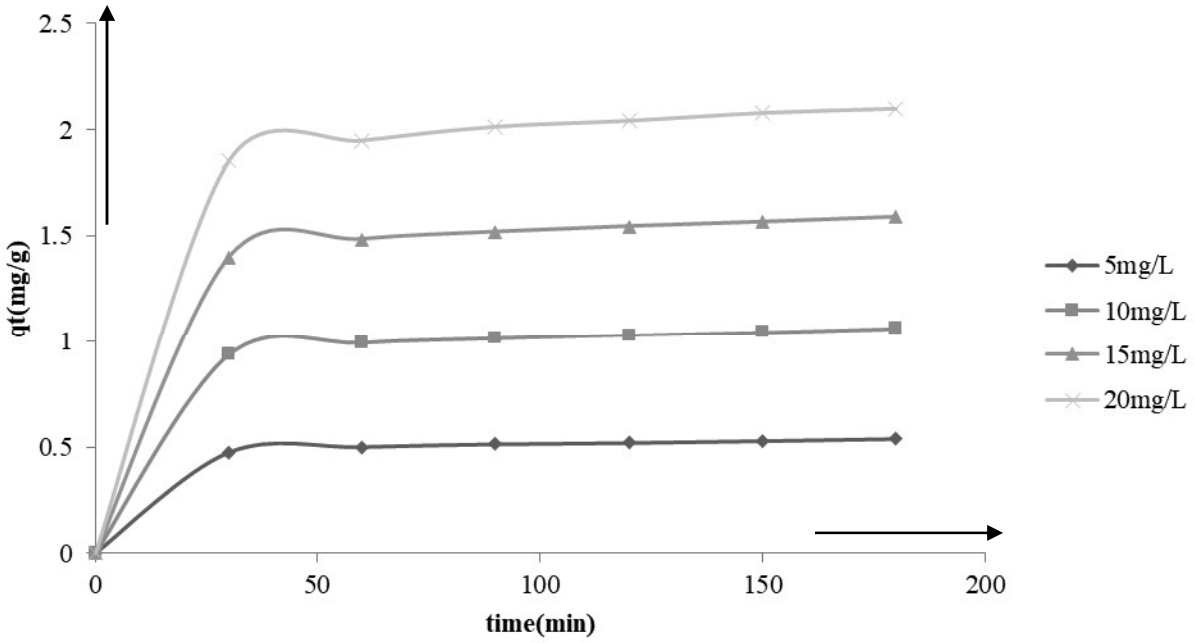

Fig. 7: Effect of contact time for Pb(II) ions removal by MCA

Effect of Initial Ion Concentration

The effect of initial concentration on the extent of adsorption of Pb(II) metal ions onto MCA at m= 0.2m/L is shown in Fig.8. It was evident that metal ions removal decreased with an increase in initial concentration. This indicates that there exists a reduction in immediate solute (metal ion) adsorption, owing to the lack of available active sites required for the high initial concentration of metal ions (Kannan and Srinivasan, 1998). The actual amount of metal ions adsorbed per unit mass of MCA increased with an increase in Ci.

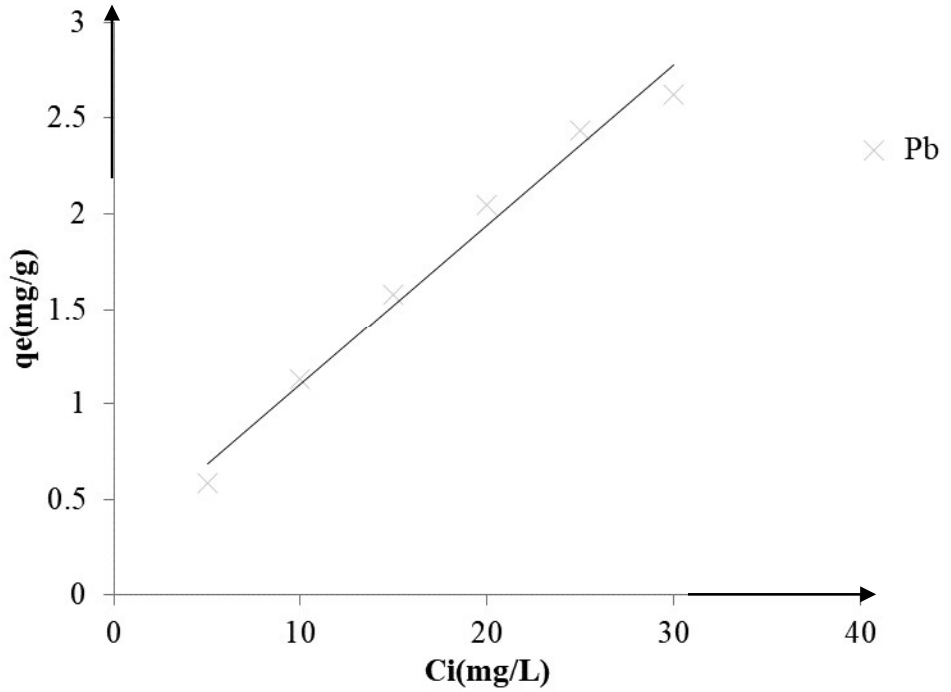

Fig. 8: Effect of initial ion concentration on Pb(II) ions removal by MCA

Effect of pH

Fig.9 showed that for metal ion Pb^{2+}, the removal by MCA decreased as the pH of the solution decreased. The critical pH value of Lead was 5.0. According to Low et al.(1995) at low pH values the surface of the adsorbent would be closely associated with hydronium ions (H_3O^+) which hinder the access of metal ion Pb^{2+} by repulsive forces to the surface functional groups, consequently decreasing the percentage of the metal Pb^{2+} removal. The increase in Lead adsorbed as pH increase can be explained on the basis of a decrease in competition between Proton (H^+) and lead ions on the surface of adsorbent. As pH increased, more adsorbent surface would be exposed and carried negative charges with subsequent attraction of lead ions (Sekar *et al,*2007).

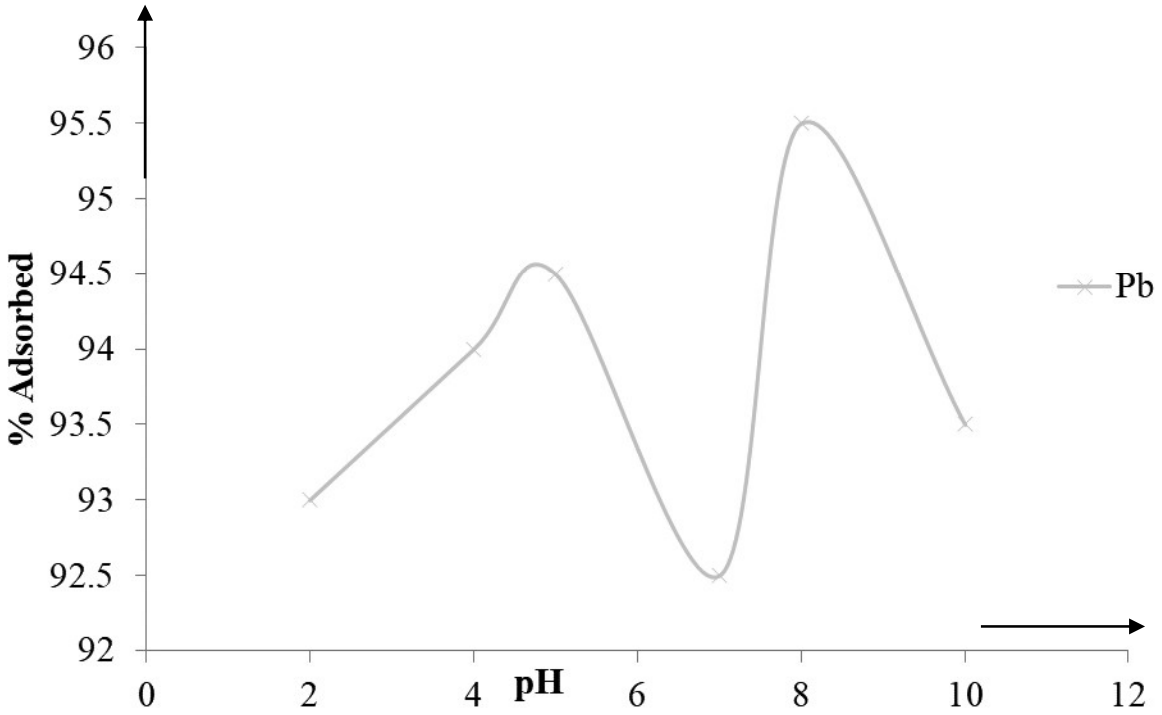

Fig. 9: Effect of pH on Pb(II) ion removal by MCA

CONCLUSION AND RECOMMENDATIONS

The kinetics of Pb (II) ions adsorption onto maize cob biomass was found to be based on the assumption of intraparticle diffusion-controlled pseudo second order mechanism with chemisorption being the predominant mechanism.

The contact time obtained in this study indicates that chemisorption is involved in the adsorption process. The adsorption of the metal's ion is pH dependent. It was noted that ionic radius has an influence in the magnitude of metal loading on the adsorbent. The adsorption capacity increases with increase in smaller ionic radius metal ion.

It is recommended that the kinetics of absorpsion of other heavy elements be carried out by subsequent researches.

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