Kinetic and Equilibrium Studies of the Adsorption of Lead(II) and Nickel(II) ions from aqueous solutions on Activated Carbon Prepared from Maize Cob

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ABSTRACT

A carbonaceous adsorbent prepared from maize cob by acid treatment has been tested for its efficiency in removing Pb(II) and Ni(II) ions. The effects of contact time, initial concentration and pH have been studied. The adsorption followed Pseudo second order reaction equation and the rate is mainly that of intra-particle diffusion. The Freundlich and the Langmuir models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from Langmuir isotherm plots for Lead and Nickel ions were 3.150 and 4.70 (mg/g) respectively. The separation factors, R_L for Pb^{2+} (0.0576) and Ni^{2+} (0.2458) were less than unity, indicating that maize cob biomass is an excellent adsorbent for the two metal ions. The adsorption coefficient, b, which is related to the apparent energy of adsorption for Pb^{2+} (0.5453L/mg) was greater than that of Ni^{2+} (0.1023L/mg). This showed that the energy of adsorption is not favourable to Pb^{2+}. Ionic radius influences the rate of adsorption of metal ion migration to the adsorbent surface. The critical pH values were both found to be 5.0 for the metal ions.

Key Words: Activated carbon, isotherms, Kinetics, diffusion and mechanism.

INTRODUCTION

The problems of our ecosystem are increasing with the advancement in technology. Heavy metal pollution is one of these problems. Toxic heavy metal release into the environment has been increasing continuously as a result of man's industrial activities and technology development. The release of these heavy metals poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature [1]. Lead is a heavy metal that affects the functioning of the blood, liver, kidney and brains of human beings. Lead is a component of most industrial and domestic paints. Nickel which causes gastrointestinal irritation and lung cancer is often obtained from Ni/Fe storage batteries. Due to the magnitude of the problem of heavy metal pollution, research into new and cheap methods of removal has been on the increase recently. Several workers have reported on the potential use of agricultural by-products as good adsorbents for the removal of metal ions from aqueous solutions and waste water [2]. This process attempts to put into use the principle of using waste to treat waste and becomes even more efficient because these agricultural by-products are readily available and often pose waste disposal problems. Hence, they are available at little or no cost, since they are waste products. This makes the process of treating waste waters with agricultural by-products adsorbents more cost effective than the use of

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conventional adsorbents like commercial activated carbon. In addition, there is no need for a complicated regeneration process when using agricultural by-products for waste water treatment [3].

The ability of some agricultural by-products to adsorb heavy metals from waste water and aqueous solutions has been reported in literature and these include: Cotton seed hulls, rice straw and sugarcane bagasse [4], Shea butter seed husk [5] and cassava fibre [6]. Also, research by Park et al [7] showed that chemical modification of agricultural adsorbents increased the sorption capacity of the adsorbent, thereby increasing the efficiency of the adsorbent.

Maize (*Zea Mays L*) is the most important cereal crop in most parts of Nigeria, particularly the Guinea Savannah zone of the country [8]. Maize is highly yielding and cheaper than other cereals. It is also a versatile crop, growing across a range of agro- ecological zones. Every part of the maize plant has economic value: grain, leaves, stalks, tassel and cob and all can be used to produce a large variety of food and non- food products [9].

The need to research on this waste and to convert them into agents of environmental control thereby reducing wastes is the justification for the present research work. This aim of this study is to investigate the kinetic behaviour, the mechanism and the equilibrium pattern of activated carbon prepared from maize cobs in the adsorption of Lead and Nickel.

MATERIALS AND METHODS

2.1 Materials
The maize cobs were collected from the Ahmadu Bello University Agricultural Research Farm, Zaria. They were cleaned to remove loose flakes then 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 in a mortar using a pestle and sieved between into fine particle sizes (1.0 and 0.8mm). The samples were stored in a clean polythene bag for analysis. From 1000mg/L stock solutions of Pb(II) from $Pb(NO_3)_2$ and Nickel(II) from $Ni(NO_3)_2.6H_2O$, working solutions of initial concentrations of 5, 10, 15 and 20mg/L of each metal were prepared using distilled water. All the reagents used where of analytical reagent grade

2.2 Activation of Adsorbent
The fraction particle size between 1.0 mm and 0.8 mm was selected and then subjected to a carbonization process in a muffle furnace at an optimum temperature of 300^oC for 4h. The samples were removed and cooled in a dessicator. A portion (2g) of the carbonised maize cob was weighed into crucible and mixed thoroughly with 2ml of 0.01M H_3PO_4 [10] at optimum conditions of temperature and time for activation. The activated carbon was then washed with deionised water and soaked in $NaHCO_3$ solution to remove any excess acid. The samples were further washed with deionised water until no acidity was left and then dried at 105^oC for 5h [11]. The dried material was ground and sieved to obtain the particle sizes between 300-850µm [12] and stored in airtight container for further experiments.

2.3 Adsorbent Characterization
The adsorbent was characterized by the testing the following properties: Bulk density [13], ash content [13] and FTIR analysis. The FT-IR spectra were recorded on a Shimatzu (FTIR-8400) Fourier Transform Infrared Spectrometer at the National Research Institute for Chemical Technology (NARICT) Zaria, Nigeria. The activated carbon samples were dried to the constant weight in an oven at 50^oC for 24h and kept in a dessicator. 1mg of the dried activated carbon was mixed with 100mg of KBr which was initially dried at 110^oC in the disk [14]. The FT-IR scanning range was 450-4000cm^{-1}. All spectra were presented without baseline correction or normalization.

Adsorption Studies of Metal Ions Using Batch Equilibrium Technique
Adsorption studies were performed in 100ml flasks containing 25ml solutions of Lead (II) and Nickel (II) ions with different initial concentrations (from 5-20mg/L). Equal mass of 0.2g each of maize cob activated carbon with particle size of 355um were placed were added to the metal ion solutions and each sample was kept in shaker for 180 minutes at room temperature of 30^0C [15] to attain equilibrium. The flasks were removed from the shaker and final concentrations of metal ions in the solution were analysed by Atomic Absorption spectrophotometry, at a desired wavelength of each metal ions. The VARIAN Atomic Absorption Spectrometer (AAS) model spectra 30P consisting of double beam, four lamp Torrent Spectrometer with a Deuterium background corrector was used.

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Standard aqueous solutions of different elements were used to calibrate the AAS machine. The adsorption capacity at equilibrium q_e (mg/g) was calculated thus

$$Q_e = \frac{C_i - C_e)}{M} \times V$$

(2.2)

Where C_i and C_e (mg/l) are the liquid phase concentrations of metal ions at initial and equilibrium concentrations respectively. V is the volume of the solution (L) and M is the mass of dry adsorbent used (g). The effect of pH was adjusted using O.1M HCl and O.1M NaOH (2 – 10). The effect of contact time (30 – 180min) was also studied. In order to evaluate the mechanism that controls the adsorption process, several equations (i.e. pseudo-first order, pseudo second order intra-particle diffusion, Langmuir isotherm and Freundlich isotherm model equations) were tested to interpret the experimental data.

RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent

The bulk density of the activated carbon derived from maize was $0.45g/dm^3$ (Table 1). Generally, carbons with bulk density of about $0.5g/dm^3$ are adequate for sugar decolourization [13]. Activated carbon having bulk densities of $0.47-0.49g\backslash m^3$ have also widely used in purification and decolourization processes [15]. The activated carbons produced from maize cob should find use in decolourization processes. The ash content of a carbon is the residue that remains when carbonaceous material is burned off. Ash consists of mainly of minerals such as silica, aluminium, iron, magnesium and calcium, [16]. The ash content of maize cob activated carbon was found to be 8% (Table 1).

Table 1: Physicochemical Parameters of the carbon

Parameter	Maize cob
Ash content (%)	8
Bulk density g/m^3	0.4500

3.1.3 FTIR Analysis of Maize Cob

The type and net charge of functional groups bonded to the carbon surface is important in understanding the mechanism of adsorption of ionic adsorbates on activated carbons [13]. The adsorption capacity of activated carbon is influenced by functional groups on the carbon surface. The functional groups on the surface of activated carbon analysed by the FT-IR demonstrated the existence of carboxyl, hydroxyl and amine groups. The FTIR spectra of the blank and metal loaded maize cob activated carbon shown in Table 2. This demonstrates that after the adsorption the shifting occurs both to higher and lower wave numbers. This shifting indicated that there were binding processes, taking place on the surface of activated carbon [17].

Broad band 3750.26 – 3455.76cm-1 represented bonded OH groups and NH groups [18], 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 of 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 [19].

Table 2 Summary of FT-IR results from metal laden activated carbon

Peak	Original Adsorption	PB(II) Loaded diff AC	Ni(II) Loaded diff AC	Assignment
1.	3750.26	3745.10 +5.16	3740.14 +10.12	Bonded-OH
2.	3455.76	3417.16 +38.60	3438.01 +17.75	Bonded-NH
3.	2921.37	2914.50 -6.87	2921.54 -0.17	Aliphatic C-H group
4.	1952.67	1957.60 - 4.93	1952.67 +0.00	Aliphatic C-H group for anhydride C=O stretching
5.	1561.07	1452.51 +8.56	1540.40 +20.67	C=O stretching
6.	1037.01	1037.67 -0.66	1030.21 +6.80	P-O-C stretching

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3.2 Effect of Contact Time

Figures 1 and 2 reveal that 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. After elapse 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 capacities of Lead and Nickel increased rapidly in the beginning of the reaction and reached equilibrium in about 90 min. A short contact time necessary to reach equilibrium indicates that the predominant mechanism is that of chemisorption [20].
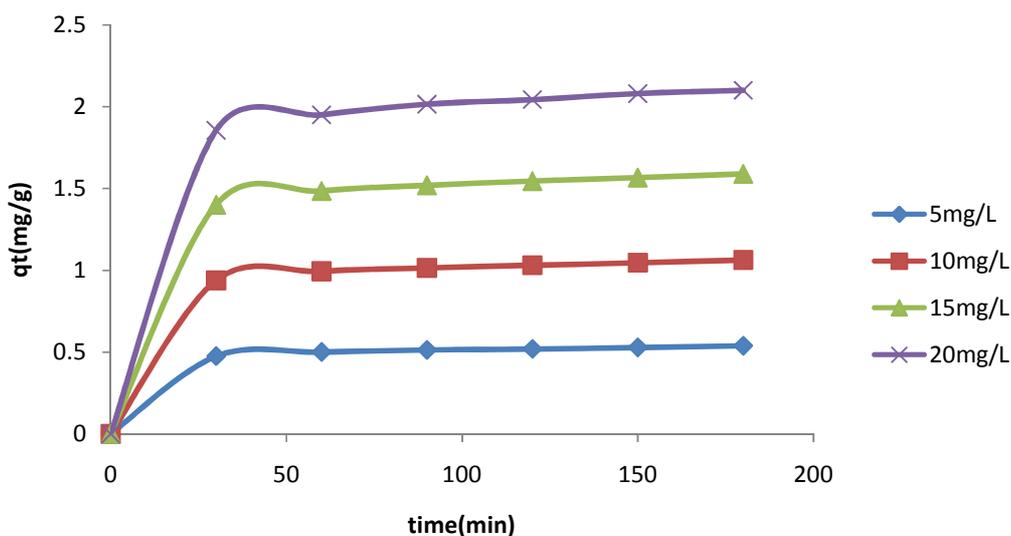
Figures 1: Effect of contact time for metal ion (Lead)
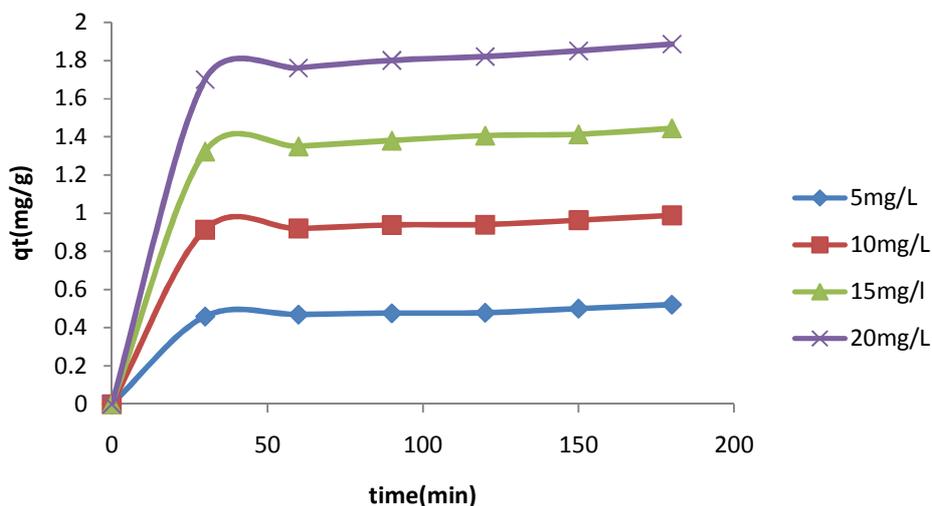
Figures 2: Effect of contact time for metal ion (Nickel)

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3.3 Effect of Initial Ion Concentration

The effect of initial concentration on the extent of adsorption of Pb (II) and Ni (II) metal ions onto Activated Maize Cob is shown in Figure 3. It was evident that metal ions removal increased with an increase in initial concentration. Figure 3: Effect of initial ion concentration

3.4 Effect of pH

The removal of metal ions from aqueous solution by adsorption is related to the PH of the solution, as the latter affects the surface charge of the adsorbents, the degree of ionisation and the species of adsorbate. Figure 4 showed that for metal ions such as Pb^{2+} and Ni^{2+}, the removal by Activated Maize Cob decreased as the pH of the solution decreased. The selection of the optimum pH takes into account the fact that, if too high a pH value is chosen precipitation would occur. This would defeat the purpose of employing adsorption [21]. The optimum pH was gotten to be 8.
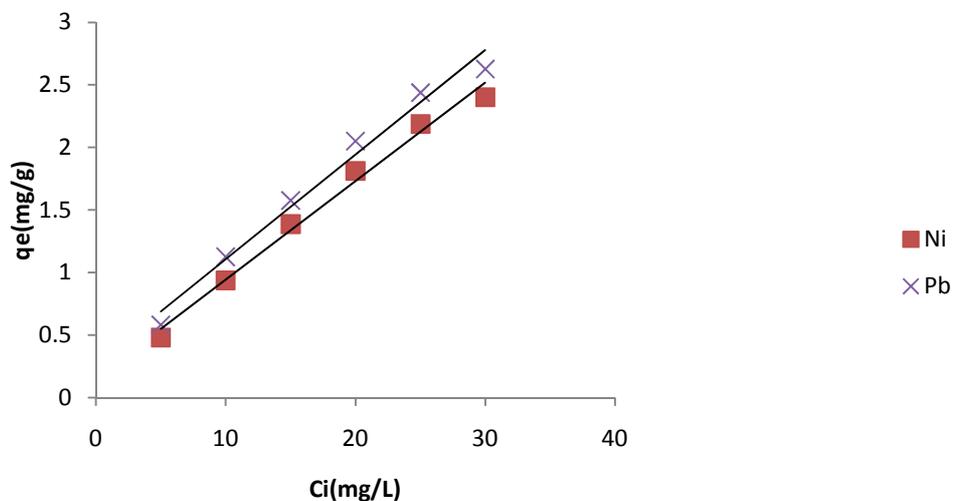
Figure 3: Effect of initial ion concentration
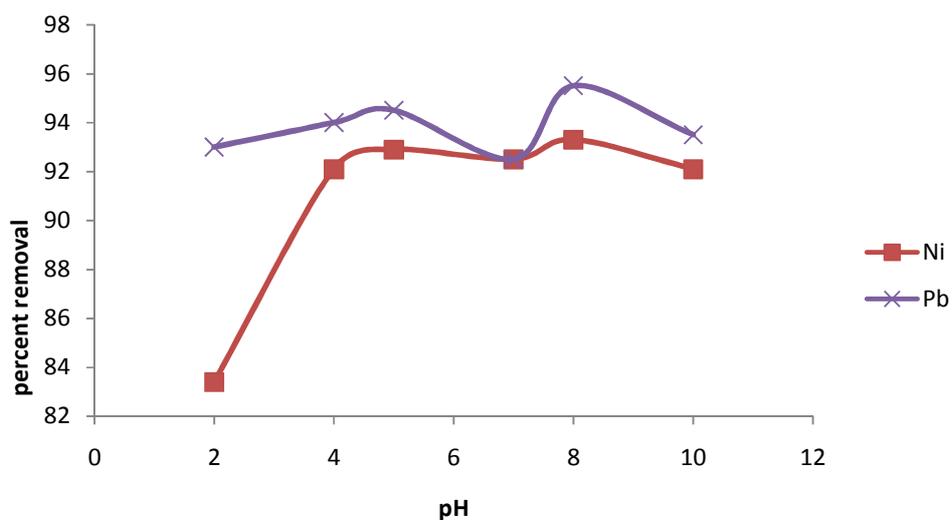
Figure 4: Effect of pH on metal ions

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3.5 Adsorption Kinetics

Frequently used kinetic models (Viz; Pseudo – first order, Largergren's first order, intra-particle diffusion and the Pseudo-second order kinetic model) have been tested to investigate the adsorption mechanism of Pb(II) and Ni (II) on activated maize cob. The experimental data best fitted into the pseudo-second order kinetic model of Ho and McKay [20] and the Largergren's first order model [25]. In the pseudo-second order kinetic model of Ho and McKay, the adsorption capacity of active sites occupied on the adsorbent and described with the expression

$$\frac{t}{q} = \frac{i}{k_2 q_e^{\,2}} + \frac{i_t}{q_e}$$

Where k_2 (g/mg – min) is the pseudo – second order rate constant. Largergren's first order kinetic equation has been widely used to describe the solute adsorption on various adsorbents, and this can be expressed as in eqn. 2.4 [25];

$$Log(q_e - q_t) = Log\, q_e - \frac{k_1}{2.303} \qquad\qquad 2.4$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbed metal ion on the adsorbent at the equilibrium and at time t, respectively and k_i (min-i) is the rate constant of first-order adsorption.

The experimental data were fitted with these two kinetic models (Figures 5-7) where, the kinetic parameters such as rate constants and equilibrium adsorption capacities of adsorption for Pb (II) and Ni (II) are summarised in Table 3. The results illustrated that a linear relationship between log (qe – qt) and t could not be obtained, indicating that first – order Largergren rate kinetics might not be appropriate to describe the adsorption. The data seemed to fit much better with the pseudo – second order kinetics. The kinetic parameters, qe and k_2 are summarized in Table 3. Extremely good agreements between the results and the model were obtained as illustrated by the R^2 for the whole range of initial metal concentrations which, by and large, confirmed the applicability of the pseudo – second order kinetics. This finding supported the assumption of the pseudo – second order model that adsorption process was due to chemisorptions [20]. In this case, chemical adsorption could have occurred by the interaction between polar functional groups on the adsorbent surface and the metals.

3.6 Intra – Particle diffusion model

The possibility of intra-particle diffusion process was explored by using the Weber and Morris intra-particle diffusion model [22].

$$q_t = k_{id} t^{1/2} + C \qquad\qquad 3.1$$

q_t = amount of metal ions adsorbed at time t (mg/g), C = intercept, k_{id} = intra particle diffusion rate constant (mg/g min$^{-1/2}$). The r-values are found to be close to unity, indicating the application of this model. The calculated values of k_{id} for the two systems were maximum for Pb(II) (0.015) and minimum for Ni(II) (0.0087). The intra particle diffusion plots are given in Figure 5. The values of intercept (*I*) give an idea about the boundary layer thickness i.e. the larger the intercept, the grater is the boundary layer effect [22]. *I* values were maximum in Pb(II) (0.8694) and minimum in Ni(II) (0.8591) indicating that the boundary layer effect is maximum in Pb(II) and minimum in Ni(II).

Table 3 : Weber And Morris Intra-Particle Diffusion for The Removal of Pb(II) and Ni(II)

Constants	Pb(II)	Ni(II)
K_{id}(mg/g min)	0.015	0.087
I (mg/g)	0.8694	0.8591
R^2	0.9797	0.8331

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Figures 5: Weber and Morris intraparticle diffusion plot for the removal of Pb(II) and Ni(II)
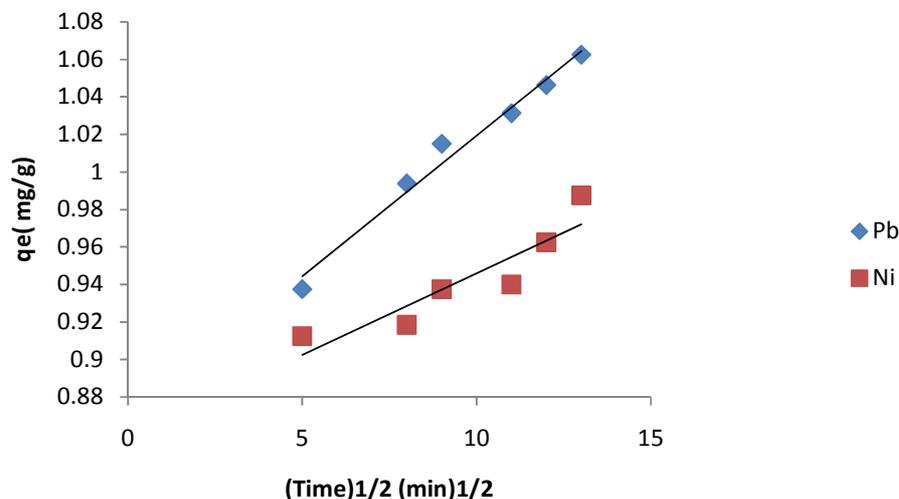
Figures 6: The correlation of the values of Log(R%) and Log(time) for the Pb(II) and Ni (II)
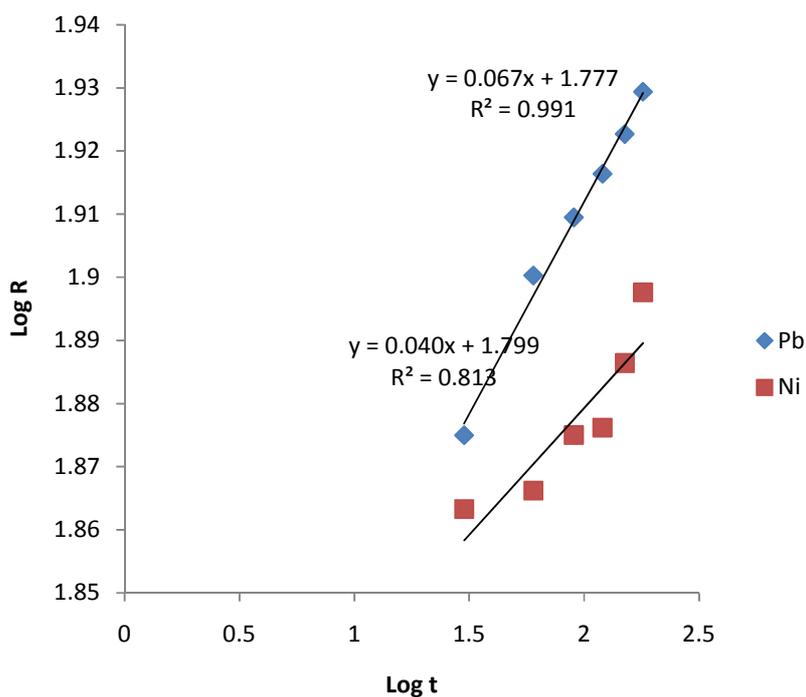
The values of log (% removal) and log (time) also illustrated a linear relationship which indicates that the process of intra particle diffusion, is taking place in these adsorption system. The divergence in the values of slope from 0.5 (min – max = 0.0402 – 0.0673) indicates the process of intra particle diffusion process as one of the limiting steps, besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously.

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Table 4: The Correlation Of The Values Of Log (% Removal) And Log (Time) For The Pb(II) and Ni(II) Ions

	Pb(II)	Ni(II)
Slope	0.0673	0.0402
Intercept	0.2498	0.2550
R – Values	0.9914	0.8138

3.7 Adsorption Isotherms

The adsorption isotherms of Pb (II) and Ni (II) ions on activated carbon are illustrated in Figures 7-10. Adsorption isotherm is relationship between adsorption capacity and concentration of the remaining adsorbate at constant temperature. Generally, there are two mathematical expression used to describe the isotherm of the adsorption, the Langmuir and Freundlich equations [23] is equation (3.2)

$$\frac{C_e}{Qe} = \frac{1}{Q_m} + \left(\frac{C_e}{bQ_m}\right) \hspace{3cm} 3.2$$

Where Q_m is the maximum adsorption capacity, b is the Langmuir constant, Q_e is the amount adsorbed at equilibrium (mg/g). The linear plots of C_e/Q_e versus Ce suggest the application of the Langmuir isotherms (Figures 7 and 8) values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table 6. Q_m is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that the maize cob had a higher adsorption capacity for Ni^{2+} (4.780 mg/g) than Pb^{2+} (3.150mg/g). The adsorption coefficient, b that is related to the apparent energy of adsorption for Pb^{2+} (0.5453 L/mg) was greater than that of Ni^{2+} (0.1023 L/mg). This observation showed that the energy of adsorption is not favourable to Pb^{2+} probably due to its large ionic radius, hence not all binding sites may be available to Pb^{2+}.

Furthermore, the extent of adsorption of the two metals on the maize cob biomass was tested using – the essential features of the Langmuir isotherm model, expressed in terms of a dimensionless constant called separation factor R which is defined by the following relationship

$$R_i = \frac{1}{1 + bC_i} \hspace{3cm} 3.3$$

Where b is the Langmuir isotherm constant C_i is the initial metal ion concentration. In the present study the values of R_L (Table 5) are observed to be fractions i.e., in the range of zero to one which indicates that the adsorption process is favourable for the two metal ions.

$$(C50.0576 – 0.2458) \hspace{3cm} 3.4$$

Freundlich isotherm equation

$$Log\ q_e = log\ K_f + 1/n\ log\ C_e \hspace{3cm} 3.5$$

Where K = adsorption capacity, $(1/n^+)$ order/intensity of adsorption, Q_e = amount of metal ions adsorbed per unit mass of adsorbent (mg/g) and C_e = equilibrium concentration of metal ion (mg/L).

The Linear plot of log q_e vs. log C_e shows that the adsorption of metal ions onto the maize cob follows the Freundlich isotherm model (Figures 9 and 10). It also indicates that the average energy of adsorption decreases with increasing adsorption intensity. Values of K_f and n were calculated from the intercept and slope and are given in Table 5 along with the Langmuir constants, the values of n between 1 and 10 represent good adsorption of the adsorbate onto the adsorbent [24].

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Figures 7 : Langmuir isotherm plot for Pb
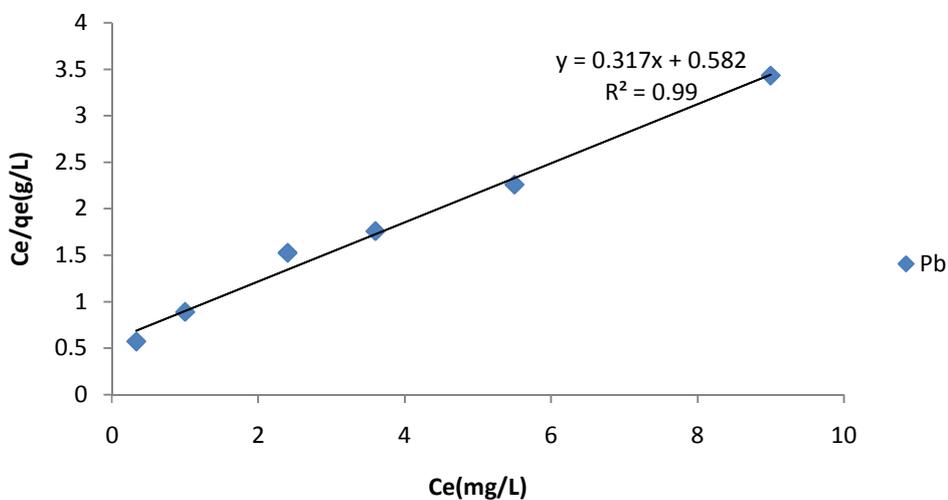
Figures 8 : Langmuir isotherm plot for Ni
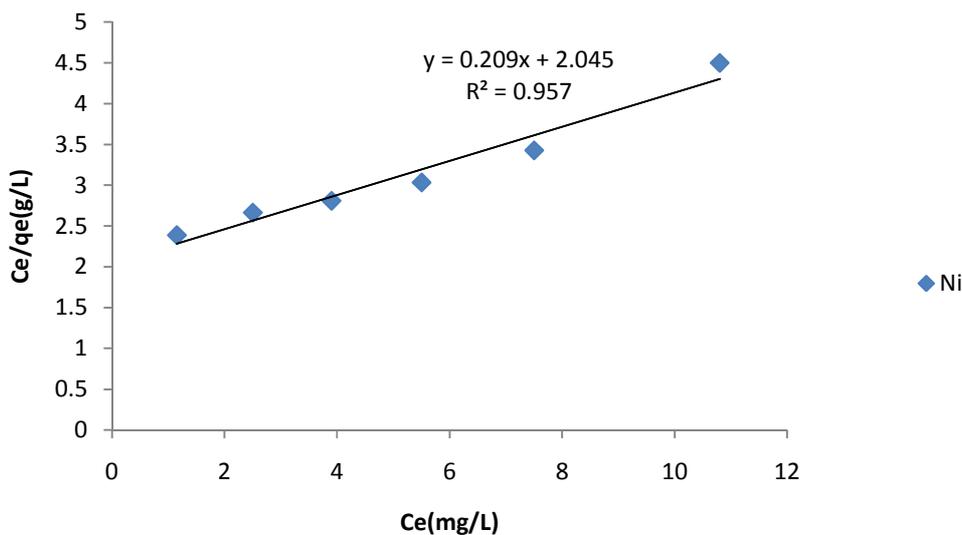
Table 5: Sorption Isotherm Constants and Coefficients of Maize Cob

Adsorbates	Langmuir Constant				Freundlich Constant		
	Q max (mg/g)	b(L/mg)	R^2	R_L	K_F(mg/g)	n	R^2
Nickel	4.70	0.1023	0.9572	0.2458	0.4671	1.3407	0.9789
Lead	3.150	0.5453	0.99	0.0576	1.0488	2.1368	0.9818

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y = 0.468x + 0.020
R² = 0.981
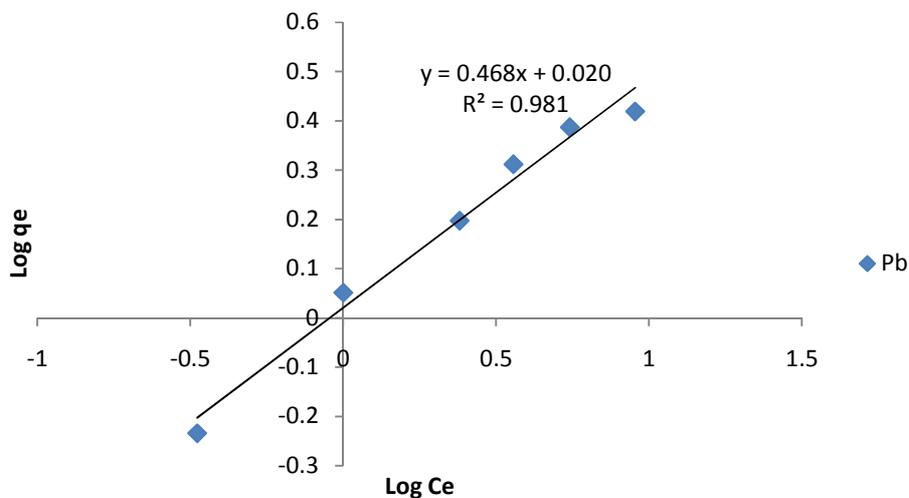
Figures 9: Freundlich isotherm plot for Pb

y = 0.745x - 0.330
R² = 0.978
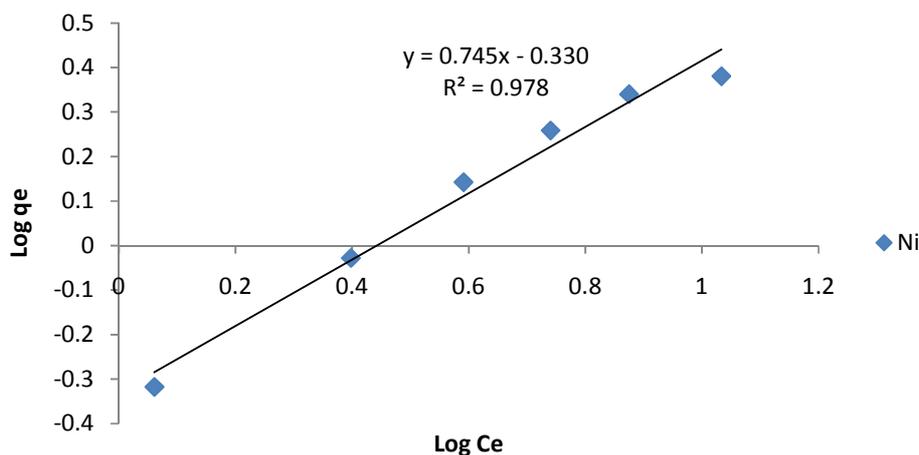
Figure 10: Freundlich isotherm plot for Ni

CONCLUSION

The mechanism of Pb(II) and Ni(II) adsorption onto maize cob biomass was found to be based on the assumption of intra-particle diffusion, controlled Pseudo second order mechanism with physisorption being the predominant mechanism. A short contact time necessary to reach equilibrium indicates that the predominant mechanism is chemisorptions. The adsorptions of metal ions are pH dependent. It was noted that ionic radius of metal ion has an influence in the magnitude of metal loading on the adsorbent.

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