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# KINETICS STUDIES OF THE REMOVAL OF MANGANESE, CADMIUM AND LEAD FROM AQUEOUS SOLUTION USING COCOA SHELL

**A. O. ERUOLA[1], C. C. OJIODU[1] AND R. A. OLOWU[2]**

[1]Department of Chemical Science, Yaba College of Technology, P.O. BOX 1775, Sabo - Yaba, Lagos, Nigeria
[2]Chemistry Department, Lagos State University, Ojo - Lagos, Nigeria
[Ojiodu1966@yahoo.com]

***ABSTRACT***

*The kinetics of the removal of manganese cadmium and lead in aqueous solution using cocoa shell as an adsorbent was investigated. The effect of contact time, kinetic of sorption mechanism and the adsorbate concentrations on sorption of $Mn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ ions were examined. The kinetic of the sorption mechanism of $Mn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ was evaluated using pseudo-first order (Lagergren) rate and the pseudo-second (Ho-model) rate model. The rate limiting sorption step was physisorption and results indicate that pseudo-second order model provides a more appropriate description of the adsorption rate for the metals ions sorption in cocoa shell. The maximum adsorption capacities per unit gram of the adsorbent at equilibrium time, neutral pH, 200 r p m, and temperature of 25 $^0C$ are 9.02 to 40.04 mg $kg^{-1}$ for $Mn^{2+}$, 7.02 to 25.89 mg $kg^{-1}$ for $Cd^{2+}$ and 5.25 to 11.01 for $Pb^{2+}$ under 10 to 50 mg $kg^{-1}$ initial metal concentration. Sorption equilibrium isotherm was determined and correlated with Langmuir and Freundlich model. It was found that the Freudlich adsorption model best fitted the isotherm data. It is concluded that cocoa shell can be use as an effective adsorbent for removal of heavy metals from aqueous solution.*

***Keywords:*** *Kinetics Cadmium, Manganese, Lead, cocoa shell, sorption.*

## INTRODUCTION

Kinetics study is important in any adsorption process and helps to identifying the type of adsorption, reaction pathway, capacity of adsorbent and reaction rate of the system. The kinetic data are essential for scaling up of sorption processes for industrial preparations. Kinetic studies on the adsorption of contaminants using different biomaterials have been reported previously[1,2] . Heavy metals are group of non biodegradable high density elements. They are released by a human of anthropogenic emission in the environment are some of the major pollutants of soil and water resources[3] . Some metals such as copper, zinc and iron are considered bio-essential while others such as cadmium, lead, mercury, manganese and chromium are highly toxic. However, even bi-essential metals may cause physiological and ecological problems if present at significant concentration. Heavy metals ions should be removed at the source in order to avoid pollution of natural water and subsequent metal accumulation in the food chain. Various physical and chemical techniques for removing metals ions from the wastewater include chemical precipitation, adsorption, ion exchange, extraction and membranes processes chemical precipitation is most common utilized conventional technique. However, the application of these methods is often limited due to their inefficiency, high capital investment or operational costs. Consequently, there is a growing requirement for novel, efficient and cost effective techniques for the remediation of metal bearing waste water before their discharge into the environment. Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from waste water and water supply[4] . Biosorption technology, utilizing natural metals or industrial and agricultural wastes to remove metal form aqueous media, often an efficient and cost-affordable alternative compound to traditional chemical and physical remediation and decontamination technique since the cost of this process are rather expensive, the use of agricultural residue or industrial by product have been studied. These agricultural waste materials includes maize bran[5] , coffee husks[6] , rice straw [7] , sugar peat pulp [8] ,olive pomace[9] , apple wastes [10] , palm kernel fibre [11] ,peanut hull [12] , hazelnut husks[13] ,oak sawdust[14] and grape stalks[15].

Despite the relative simplicity and potential cost effectiveness of bio sorption, metal removal using low cost bio-sorbents is relatively improve and need further development before it may be applied routinely in practice and thus considered an alternative to use of ion-exchange resins or activated carbons. Cocoa shell is an abundant agricultural waste product with millions of tons being generated annual polluting the environment in Nigeria. The cocoa shell has been recognized to have significant potential as a biosorbent for metal removal after simple pre-treatment. In this work, we investigated the potential of cocoa shell to act as a bio sorbent for $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ removal from aqueous media.

## MATERIALS AND METHODS

### Sorbent preparation

The cocoa shell collected locally, dried, grinded into powdered and sieved through 450 µm and 300 µm mesh screens. The portion of the cocoa shell retained on the 300 µm mesh was steeped in dilute nitric acid solution for 8 hours rinsed with deionized water and air dried.

### Sorbate preparation

1000 mg $kg^{-1}$ of each of each metal stock was prepared by dissolving calculated amount equivalent of 1.00g of each metal in a specific compound ($MnSO_4.H_2O$,

$CdSO_4$ and $Pb(NO_3)_2$) in 1litre distilled water (1000mg/L). Standard $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ solutions of 10, 20, 40 and 50 mg $kg^{-1}$ were prepared serially by diluting the stock solutions respectively.

**Contact time study**

Equilibration time for the adsorption and adsorptions model of $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ on cocoa shell was carried out on the metals ions. 30 ml of each selected concentration of salt solutions of heavy metals in distilled water were added each into 1g of cocoa shell meal weighed into shaking bottles at room temperature (25°C) under neutral pH each to determine the time required for each of the metal ion to reach adsorption equilibrium. Two drops of toluene was added to each solution in the bottles to inhibit microbial growth. The shell suspensions were shaken on a mechanical shaker at a speed of 200 rpm for 40, 80, 120, 160 and 180mins. After the specified shaking time, the solution phase was filtered by using filter paper (whatman 110mm and 11mm pore size) for removing the suspended shell particles. A 10 ml of aliquot of supernant were analyzed for residual $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ respectively by Flame Atomic Absorption Spectrophotometer. The adsorbed heavy metal concentration in cocoa shell was taken as the difference between metal added in initial solution and the remaining metal in supernatant solution after equilibration. The time for metal adsorption to reach equilibrium was determined graphically from the plot of adsorption values against time of equilibrium. The adsorbed metal ions individually on cocoa shell per unit adsorbent mass was calculated as follows:

$$Q_e = (C_o - C_e)\, V/\, m \ldots\ldots\ldots (1)$$

$C_o$ is the initial heavy metal concentrations (mg/l); $C_e$ is the concentration of heavy metal at equilibrium (mg/l), m is the cocoa shell mass (m), V is the volume of solution (ml). Calculations were made by using these data and adsorption curves were obtained.

**RESULTS AND DISCUSSION**

**Effect of contact time**

The time taken to attain equilibrium for $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ at neutral pH, temperature of 25°C and centrifugation speed of 200 rpm using 1g of cocoa shell is shown in figure 1, 2, 3. It was observed that the amount of $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ adsorbed per unit mass of cocoa shell increased significantly with increase in initial concentration. The adsorbed rate was very rapid in the first few minutes after which the rate decreased sharply and eventually reached a constant peak after at 160 minutes of the adsorption irrespective of concentrations. The two stage sorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature[16]. 160 minutes was therefore indicated as the time for $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ adsorption to reach equilibrium. The necessary contact time to reach the equilibrium depends on the initial metal ion concentration. The uptake rate is controlled by the rate at which the metals ($Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$) were transported from the exterior to the interior sites of the adsorbent. The adsorption capacity was observed to increase with the initial metal concentration for the series (10, 20, 40 and 50 mg $kg^{-1}$) for the selected heavy metals .This is due to larger surface area of the cocoa shell at the beginning of adsorption reaction. The amount of the metal ion each in their different series shows the same magnitude in their removal but varies in the adsorption capacity. However, the differential sorption of $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ ions may be ascribed to the difference in their ionic sizes. The ionic sizes of $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ are 0.67, 0.97, and 1.20 respectively. The smaller the ionic size the greater its affinity to reactive sites. The adsorption capacity increased in the substrate with stronger bond for smaller size metal ion indicative that the competition of manganese with ionic radius of 0.67A has higher binding site than cadmium with ionic radius of 0.97A on cocoa shell. The lowest adsorption capacity of lead with weak bond on cocoa shell could be attributed to its highest ionic radius 1.20A. $Mn^{2+}$, $Cd^{2+}$and $Pb^{2+}$ adsorbed by complexation reaction. This general trend of the sorption is due to the fact that metal ion with smaller ionic radius diffuse faster in aqueous systems and compete better for exchange site than for those with larger sizes. This trend in smaller ionic size was also observed for $Cu^{2+}$,$Cd^{2+}$ and $Zn^{2+}$ using other biological adsorbents[17] . According to Cho *et al.* (2005)[18] metal with smaller hydrolysis constant ($Pk_H$) has the increasing tendency to hydrolyse because of their larger charge-size function ($z^2/r$). The $Pk_H$ for manganese to cadmium shows that cadmium will be hydrolyze to a greater extent than manganese indicating a higher binding for manganese > cadmium and lead has the least adsorption. So the adsorption capacities increases from $Mn^{2+} > Cd^{2+} > Pb^{2+}$. The long contact time of 160 minutes observed to reach equilibrium for all the metal ions indicated that the predominant mechanism was physisorptions which encourage easy removal of the adsorbed heavy metals or regeneration of the spent adsorbent.

**Effect of initial rate concentration**

The initial concentration provides a driving force to overcome all mass transfer resistances of the metals ion in the aqueous and solid phase. This led to higher probability of collision between the metal and active sites of the cocoa shell. The surface adsorption sites become exhausted at some point in time, it reached a constant value in which no more metal is removed from solution [19-20]. At this point, the adsorbed amount of heavy metals on cocoa shell was in a state of dynamic equilibrium[21] . The equilibrium uptake increased with the increasing of initial metal ions at the range of experimental concentration. Initial rate of the sorption capacity was greater for higher initial heavy metals concentrations, because the resistance to each of the metal uptake decreased as the mass transfer driving force increased so the initial rate of adsorption in metals was greater for higher initial adsorbate concentrations (50 mg $kg^{-1}$) than for the lowest concentration (10 mg $kg^{-1}$) of metals ions (manganese, cadmium, and lead) on cocoa shell. This agrees with the work of Okiemen et al (1987)[22] work on cadmium, lead, zinc ions in sulphur containing chemically modified cellulosic material lust.

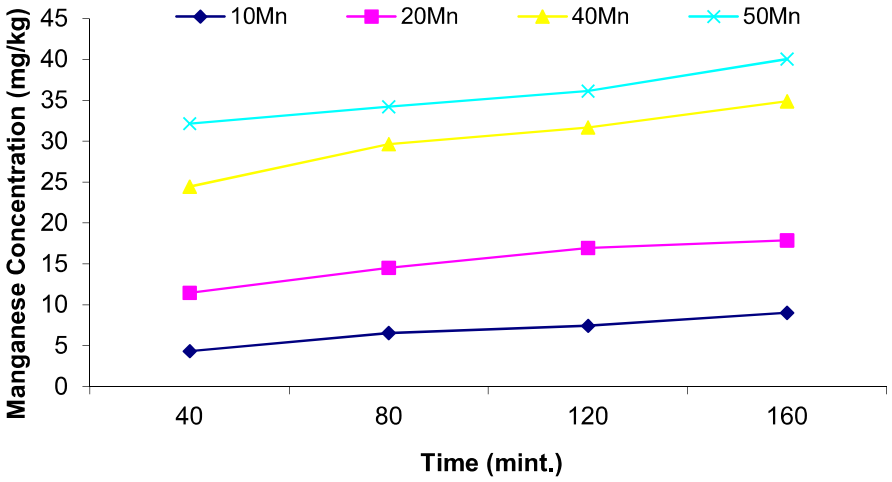


**Figure 1: Time of attainment of manganese adsorption equilibrium at pH of 7.0, 10mgkg$^{-1}$ and temperature of 25$^{o}$C and centrifugation speed of 200 rpm per unit mass of cocoa shell.**

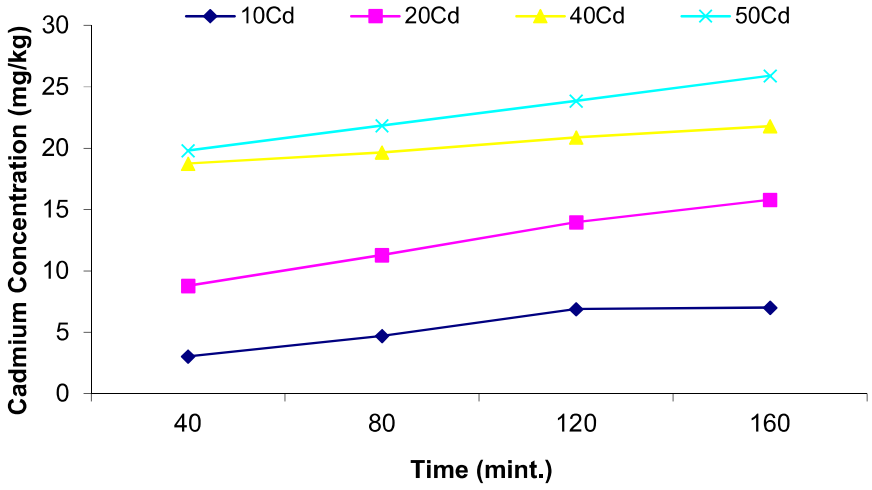


**Figure 2: Time of attainment of cadmium adsorption equilibrium at pH of 7.0, 10mg kg$^{-1}$ and temperature of 25$^{o}$C and centrifugation speed of 200 rpm per unit mass of cocoa shell.**

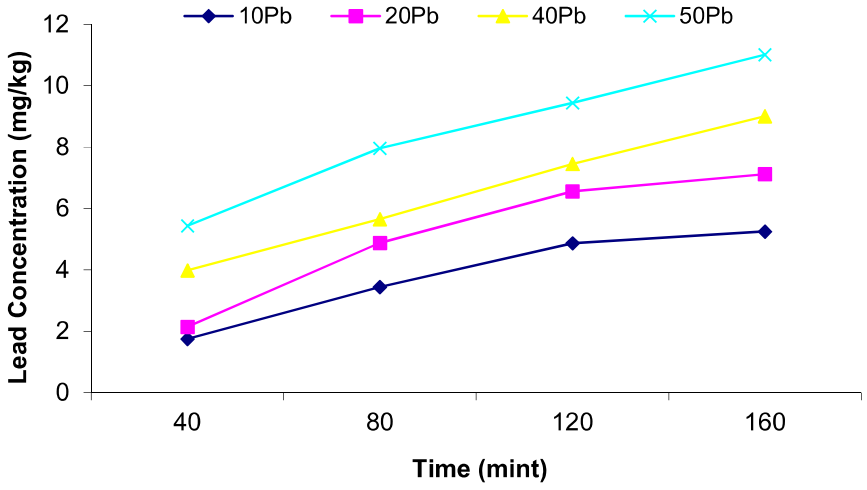


**Figure 3: Time of attainment of lead adsorption equilibrium at pH of 7.0, 10mg kg$^{-1}$ and temperature of 25$^{o}$C and centrifugation speed of 200 rpm per unit mass of cocoa shell.**

**Kinetic treatment of experimental data**

The mechanism of adsorption for the heavy metals was subjected to both pseudo-first order Lagergren, (1898)[23] and pseudo second order Ho and Mckay (1999)[24] equations at the initial metal concentrations of 10 mg $kg^{-1}$

**Pseudo first order or Lagergren equation**

$\text{Log } [Q_e - Q] = \log Q_e - k_1/2.303_t$ ……..(2)

A linear plot of log $[Q_e - Q]$ against 't' indicates the conformity with the model

$Q_e$ = mass of metal adsorbed at equilibrium (mg $kg^{-1}$)

Q= mass of metal adsorbed at time "t" (mg $kg^{-1}$)

"t"= time for adsorption (hrs)

$k_1$ = equilibrium rate constants for $1^{st}$ order

**Pseudo second order or Ho (2004) equation**

$t/Q_e = 1/k_2Q_e^2 + t/Q_e$ ……..(3)

A linear plot of $t/Q_e$ against't' indicates conformity with the model

$Q_e$ = mass of metal adsorbed at equilibrium (mg $kg^{-1}$)

"t"= time for adsorption (hrs)

$k_2$ = equilibrium rate constants for $2^{nd}$ order.

First order kinetics for $Mn^{2+}$, $Cd^{2+}$and $Pb^{2+}$ onto maize cob are shown in Figure 4, 5, 6.

Figures 7, 8, and 9 illustrates the pseudo second order (Ho) equations of $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ respectively at the initial metal concentrations of 10 mg $kg^{-1}$.

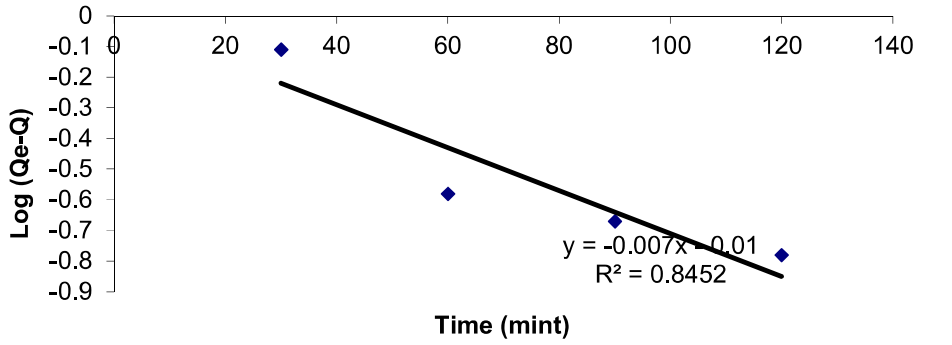


**Figure 4: Lagergren pseudo first order kinetic plot for manganese at pH of 7.0, initial metal concentration of 10mg $kg^{-1}$ and temperature of 25°C per unit mass of cocoa shell.**

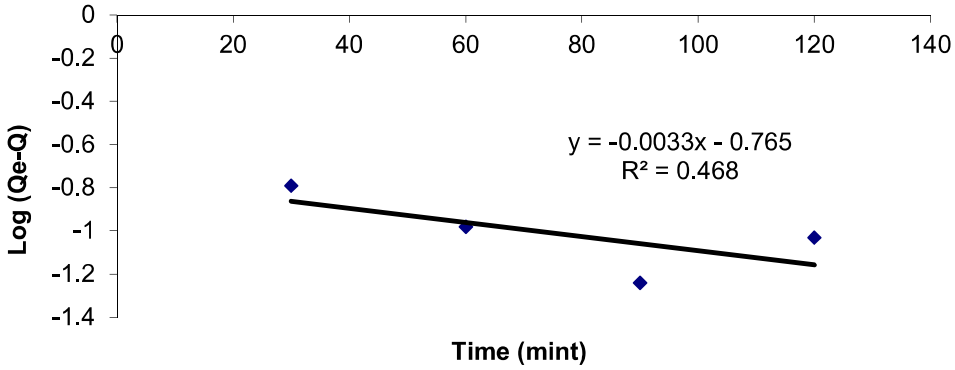


**Figure 5: Lagergren pseudo first order kinetic plot for cadmium at pH of 7.0, initial metal concentration of 10 mg $kg^{-1}$ and temperature of 25°C per unit mass of cocoa shell.**

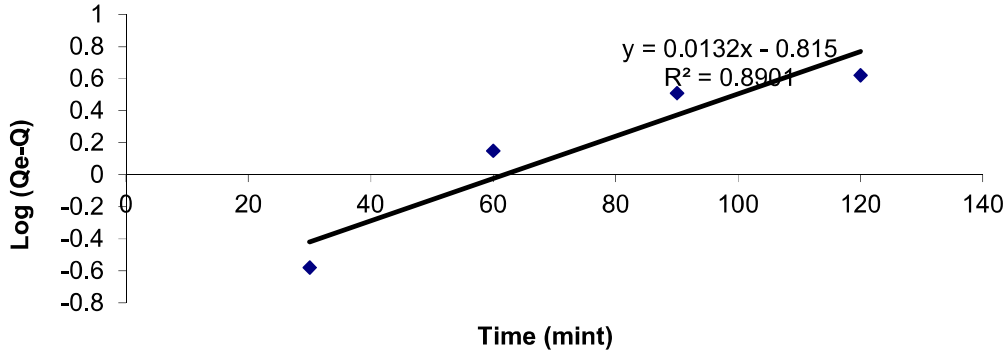


**Figure 6: Lagergren pseudo first order kinetic plot for lead at pH of 7.0, initial metal concentration of 10 mg $kg^{-1}$ and of 25°C per unit mass of cocoa shell.**

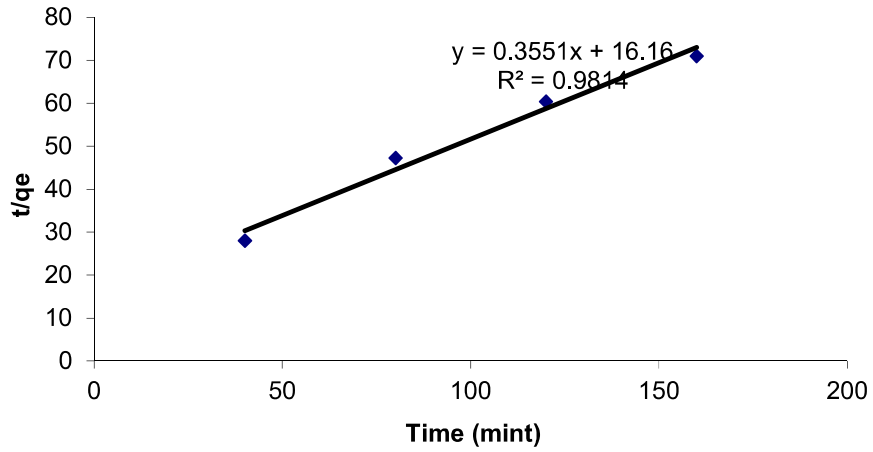


**Figure 7: Ho pseudo second order kinetics plot for manganese at pH of 7.0, initial metal concentration of 10 mg $kg^{-1}$ and 25°C per unit mass of cocoa shell.**

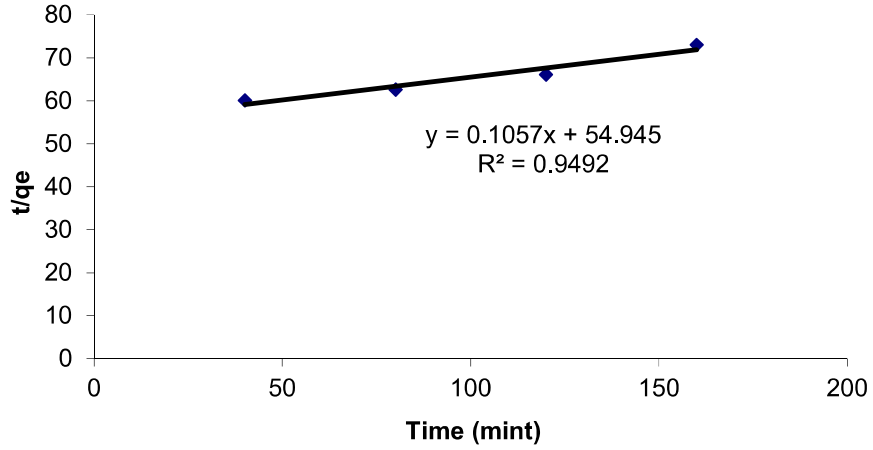


**Figure 8: Ho pseudo second order kinetics plot for cadmium at neutral pH, initial metal concentration of 10 mg $kg^{-1}$ and 25°C per unit mass of cocoa shell.**

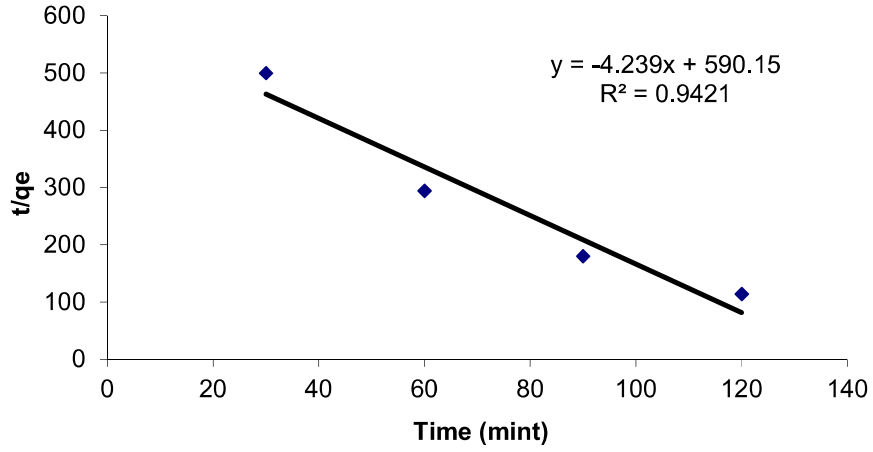


**Figure 9: Ho pseudo second order kinetic plot for lead at neutral pH, initial metal concentration of 10 mg $kg^{-1}$ and 25°C per unit mass of cocoa shell.**

The rate of the metals sorption has the highest conformation with pseudo second order (Ho) rate model each, with coefficient of determination ($R^2$) of 0.98, 0.95and 0.94 for $Mn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ respectively.

**Adsorption isotherms**

The adsorption characteristics of manganese, cadmium and lead was determined by fitting the adsorption data into both Freundlich (1926) and Langmuir (1918) equations respectively.

**Freundlich isotherm:** This is use for modeling the adsorption on heterogenous surfaces. This can be explained by the equation

$Q_e = K_f C_e^{1/n}$ **……(4)**

The linear form of equation (4) can be written as:

$\text{Log } Q_e = 1/n \log C_e + \log k_f$……..(5)

$Q_e$ = the quantity of ions absorbed per unit weight of absorbent.

$C_e$ = the equilibrium concentration of the adsorbate after adsorption has taken place.

"$K_f$" = Freunlich constant; and "1/n" = adsorption intensity.

$Mn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ adsorption isotherm using Freundlich approach in the study is presented as a function of the equilibrium concentration of metal ions in the aqueous medium at neutral pH, 25°C and contact time of 160 minutes is shown in Figure 10, 11 and 12. These adsorptions gave a linear fit form of the model with the coefficient of determination ($R^2$) of 0.96, 0.96 and 0.96 for $Mn^{2+}$, $Cd^{2+}$and $Pb^{2+}$ which are strong correlation.

The Freundlich adsorption co-efficients ($k_f$ and 1/n) were numerical values that characterized the cocoa shell surface for its affinity for the metals. All the metals exhibited a slope (1/n) defined as adsorption intensity which is less than unity thereby exhibiting a favourable condition for the cocoa shell surface which agrees with Horsfall and Abia (2003) [25]. The 1/n that was less than unity implies that the surface site heterogeneity was predominant for the adsorption of the metals on cocoa shell that is, there was broad distribution of adsorption of the ions on the cocoa shell. The adsorption capacity ($k_f$) for $Mn^{2+}$, $Cd^{2+}$and $Pb^{2+}$ by cocoa shell were positive value which predicted that the quantity adsorbed on cocoa shell corresponds to complete heterogenous layer coverage.

**Langmuir adsorption isotherm:**

This model suggests that the uptake occurs on homogenous surface by monolayer sorption with interaction between sobbed molecules. The model assumed uniform energies of adsorption onto the surface. Langmuir isotherm can be defined according to the following

$\mathbf{Q_e == V_m k C_e / 1 + k C_e}$……(6)

$Q_e$ = the quantity of ions absorbed per unit weight of absorbent.

$C_e$ = the equilibrium concentration of the adsorbate after adsorption has taken place.

$V_m$ is the monolayer capacity and "k" is the equilibrium constant.

The linear form of equation (6) can be written as follow:

$\mathbf{C_e/Q_e = 1/kV_m + C_e/V_m}$……(7)

The sorption of the metals ions ($Mn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$) on cocoa shell also showed linearity with Langmuir linear equation. This indicates that the adsorption in $Mn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$did occur at the homogeneous surface molecules to each other as well in the plane of the active site cocoa shell.

**CONCLUSION**

This study clearly suggest that the use of cocoa shell as sorbent is much economical, effectual and more viable. It can be efficiently used to remove ions from aqueous solution. The different operational parameters observed during the process of investigations reveal that the adsorption of manganese, cadmium and lead ions was dependent on initial rate concentrations, ionic strength and contact-time with same magnitude in their removal but different adsorption capacities.

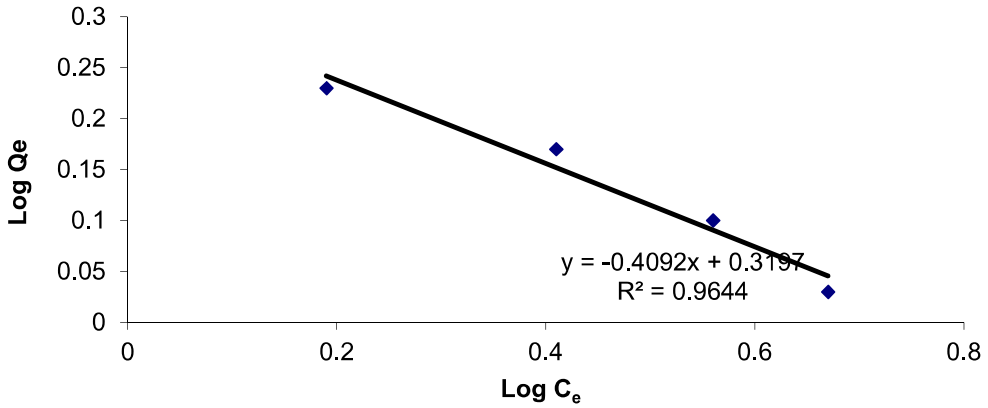


**Figure 10: Freundlich adsorption isotherm for manganese at neutral pH, 10 mg $kg^{-1}$ initial concentration and 25°C per unit mass of cocoa shell.**

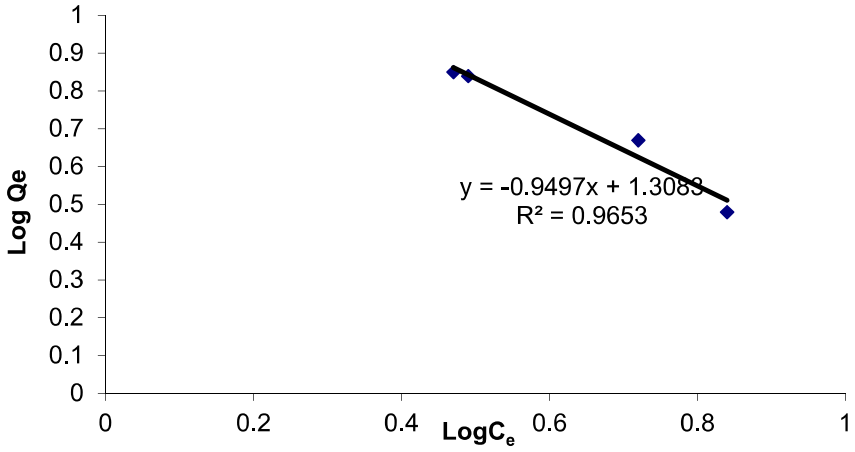


**Figure 11: Freundlich adsorption isotherm for cadmium at neutral pH, initial concentration of 10 mg $kg^{-1}$ and 25°C per unit mass of cocoa shell.**

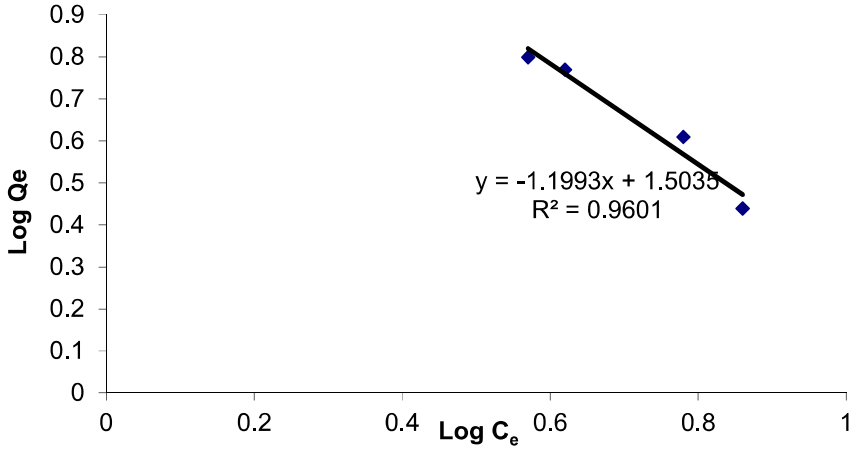


**Figure 12: Freundlich adsorption isotherm for lead at neutral pH and initial concentration of 10 mg $kg^{-1}$ and 25°C per unit mass of cocoa shell.**

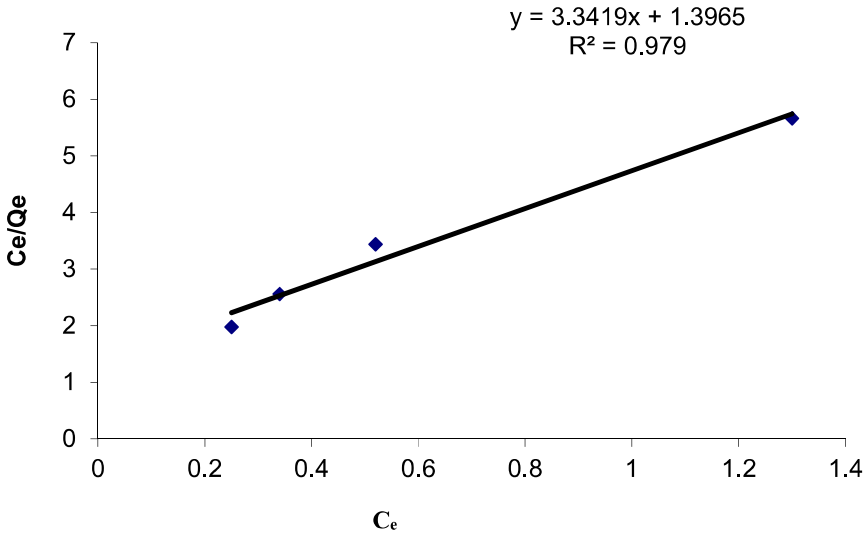


**Figure 13: Langmuir adsorption isotherm for manganese at neutral pH and initial concentration of 10 mg $kg^{-1}$ and 25°C per unit mass of cocoa shell.**

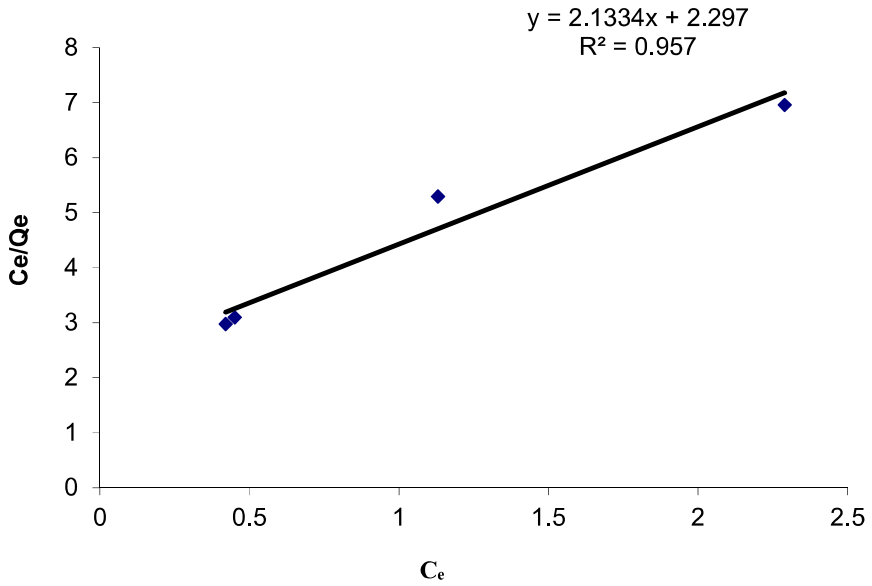


**Figure 14: Langmuir adsorption isotherm for cadmium at neutral pH and initial concentration of 10 mg kg$^{-1}$ and 25$^{o}$C per unit mass of cocoa shell.**

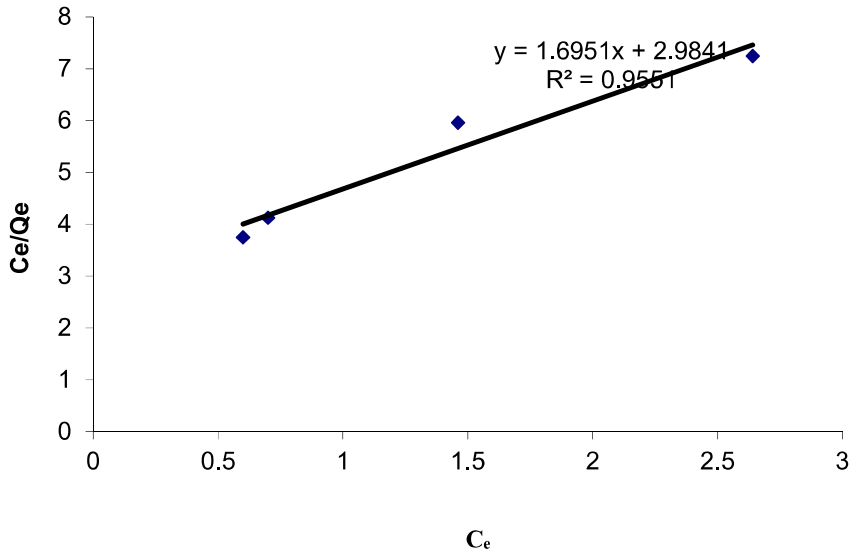


**Figure 15: Langmuir adsorption isotherm for lead at neutral pH and initial metal concentrations of 10 mg kg$^{-1}$ and 25$^{o}$C per unit mass of cocoa shell.**

The long contact time of 160 minutes at which equilibrium for manganese, cadmium and lead ions was reached indicated that the predominant mechanism is physisorption and the kinetic of their reactions is best described by pseudo- second order rate model. It is common to describe the goodness of it in terms of $R^2$, which is the square of the correlation coefficient. Both Langmuir and Freundlich isotherms shows an adequate fit of experiment data in the whole range of concentrations generally giving the $R^2$ values higher than 0.90. The ability of these models to represent the experiment data could have been due to the fact that the isotherms take into account adsorbent-adsorbate interactions. The adsorption of the metals ions conform with Langmuir and Freundlich isotherm of both heterogeneous and homogenous adsorptions on the adsorbent surface. The adsorption capacities decreases from $Mn^{2+}$, $Cd^{2+}$and $Pb^{2+}$ respectively. As a result of this study, it may be concluded that cocoa shell may be used as alternative and effective material for elimination of heavy metal pollution from waste waters since it is low cost, abundant and locally available adsorbent.

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