

# Sorption studies on the use of african breadfruit (*Treculia africana*) seed hull as adsorbent for the removal of $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ from aqueous solutions

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**Abstract:** The sorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solutions by unmodified (UBSH) and modified (MBSH) African breadfruit (*Treculia africana*) seed hull has been investigated. The amount of ions adsorbed by the hulls was dependent on the contact time range, 10 min – 120 min at optimum pH, 7.5 and temperature, 30 °C. Results revealed that the amount of metal ions adsorbed increased with time for both UBSH and MBSH, as well as a slight drop in the amount of  $\text{Cd}^{2+}$  adsorbed between contact time 60 min and 90 min for only UBSH. The rate of removal of the metal ions from their solutions was rapid, as appreciable amounts (96 % – 99 %) were adsorbed by the adsorbents at the least contact time (10 min) of the experiment. However, sorption capacity trend of the metal ions was  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$  for both UBSH and MBSH. Modification by thiolation of the adsorbent showed enhancement mainly in the sorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  and a reduction for  $\text{Pb}^{2+}$  due to low affinity of  $\text{Pb}^{2+}$  for –SH groups. A comparison of kinetic models applied to the sorption process was evaluated for Pseudo-first order and Pseudo-second order models, with Pseudo-second order providing a better fit to the experimental data with high  $R^2$  values ranging 0.9999 to 1. McKay & Poot intraparticle diffusion model also provided a good fit to the experimental data with more  $R^2$  values close to 1 than Weber & Morris model, thus suggesting the sorption process to be intraparticle diffusion controlled. Generally, the results from this study, indicates that a good adsorbent can be obtained from both unmodified and thioglycollic acid-modified breadfruit seed hull.

**Keywords:** African Breadfruit Seed Hull; Aqueous Solution; Intraparticle Diffusion; Kinetics; Metal Ions; Sorption; Thiolation

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## 1. Introduction

The increasing pace of industrialization, mining of metallic ores, smelting and extrusion of metals, widespread and indiscriminate dumping of metallic compounds, vehicular emissions etc. have led to metal contamination of the aquatic ecosystems. The pollution of an aquatic environment can alter its physical, chemical and biological characteristics, thereby jeopardizing the quality of water for industrial, agricultural and domestic uses [1]. Of the variety of existing pollutants, heavy metals have received special attention since some of them are extremely harmful to a large variety of organisms when they exceed tolerable limits permitted by environmental legislation [2].

Contamination of water by heavy metals ions contributes to several health hazards. Lead for instance, can interfere

with enzyme activities and formation of red blood cells. It can affect nerves and brain at low concentration [3]. Cadmium is responsible for kidney tubular impairment and osteomalacia, among other health problems associated with its exposure [4]. The presence of copper (II) ions can cause serious toxicological concerns, it is usually known to deposit and cause damage in the brain, skin, liver, pancreas, and myocardium [5]. Since most of the heavy metals are non-degradable into non-toxic end-products, their concentrations must be reduced to acceptable levels before discharging them into the environment. Otherwise these could pose threats to public health when they enter the food chain. According to World Health Organization (WHO), the metals of most immediate concern are chromium, copper, zinc, cadmium, iron, mercury and lead [6]. Consequently, removal of heavy metals from wastewater is of primary importance because they are not only causing contamination

of water bodies. Nonetheless, they are also toxic to many life forms. In view of these effects, hence the urgent need for the removal of heavy metals from their solutions.

Conventional methods for heavy metal removal from wastewater /aqueous solution include chemical precipitation, electrolytic recovery, ion exchange, chelation and solvent extraction /liquid membrane separation [7]. But these methods are often most cost prohibitive, having inadequate efficiencies at low metal concentrations particularly in the range 1 – 100 mg/L [8]. Furthermore, some of these methods generate toxic sludge, the disposal of which is an additional burden on the techno-economic feasibility of treatment procedures. These constraints have caused the search for alternative methods that would be efficient for metal sequestering. Such a possibility offers a method that uses adsorbents of biological origin for removal of heavy metals from dilute aqueous solutions. Among these adsorbents are agricultural waste-products that make wastewater treatment more cost effective than the use of conventional adsorbents like activated carbon. Several researchers have therefore reported on the use of many agricultural waste-products as good substrates for the removal of metal ions from aqueous solutions and wastewaters. Some of these adsorbent materials include petiolar felt-sheath of palm [9], rice husk [10], wheat shell [11], bengal gram husk [12], waste sugar beet pulp [13], oil palm fruit fibre [14], saw dust [15], maize cob [16], cassava fibre [17], arca shell biomass [18], dyed cassava mescocarp [19], coconut fibre [20], cocoa pod husk [21, 22], sand paper leaves [23], coconut shell/baggase [24], among others.

The present article reports the feasibility of utilizing African breadfruit (*Treculia africana*) seed hull as a low cost adsorbent material for the removal of toxic heavy metal ions from wastewater. African breadfruit (*Treculia africana*) seed hull is a typical waste biomass or plant residue. Plant residues are mainly composed of highly fibrous ligno-cellulosic materials. They have relatively large surface areas that can provide intrinsic adsorptive sites to many substrates and can inherently adsorb waste chemicals such as dyes and cations in water due to coulombic interaction and physical adsorption [25]. These agricultural wastes are renewable and abundantly available at little or no cost. In the present study, the sorption kinetics of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  onto modified and unmodified African breadfruit (*Treculia africana*) seed hull was studied at optimum pH, 7.5 and temperature, 30 °C. The effect of contact time between the adsorbent and the metal ions was also investigated.

## 2. Materials and Methods

### 2.1. Preparation of Adsorbent

African breadfruit (*Treculia africana*) seed hulls were obtained from Uturu, Abia State, Nigeria. The hulls were cut into small pieces, air-dried and crushed into powdery form using a manually-operated grinder. The breadfruit

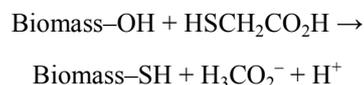
seed hull meal obtained was dried further in the oven at 50 °C. After 12 h, the meal was removed from the oven and sieved through a 250  $\mu\text{m}$  mesh screen. This portion of the breadfruit seed hull meal retained on 250  $\mu\text{m}$  mesh was used for the adsorption experiment.

### 2.2. Activation of Adsorbent

The portion of the breadfruit seed hulls meal retained on the 250  $\mu\text{m}$  mesh was then soaked in dilute nitric acid solution (2 % v/v) overnight at room temperature. After 24 h, the meal was filtered through a Whatman No. 41 filter paper and rinsed with deionized water and air dried. The adsorbent was dried again in the oven at 105 °C for 6 h. After drying in the oven, the hulls were divided into two parts; one part of the hulls was used for sorption studies without chemical modification (i.e. the unmodified breadfruit seed hull) and was labeled UBSH. The other portion was modified by the introduction of thioglycolic acid (i.e. the modified breadfruit seed hull labeled MBSH).

### 2.3. Modification of Adsorbent

The African breadfruit (*Treculia africana*) seed hull was thiolated by the method reported by Okieimen and Okundaye [26]. Specifically, a 25 g sample of the activated breadfruit seed hull was thiolated with 250 mL of 1.0 M solution of thioglycolic acid for 24 h at 29 °C. The mixture was filtered (after 24 h), washed with deionized water and then with methanol. It was finally washed with deionized water and dried at 50 °C for 12 h. This thioglycolic acid modification process led to the thiolation of the hydroxyl groups of the cellulosic biomass by the following reaction:



The degree of thiolation was estimated titrimetrically by reaction of the thiolated hull with iodine and back-titration of the unreacted iodine with sodium thiosulphate solution.

### 2.4. Preparation of Adsorbate

All reagents used were of analytical grade and were used as purchased without further purification. Doubly-distilled and deionized water was used in the preparation of all sample solutions. Stock solutions of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  metal ions of 1000 mg/L concentrations were prepared by dissolving known amounts of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), cadmium chloride ( $\text{CdCl}_2$ ) and lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), respectively in 1000 mL of deionized water. From these stock solutions, working solutions (aliquots) of 100 mg/L (initial concentration) of each metal ion were prepared by serial dilution.

## 3. Sorption Studies

Sorption studies for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were carried out for each adsorbent (UBSH and MBSH respectively) at pH,

7.5, temperature, 30 °C and initial concentration, 100 mg/L. 50 mL standard solution of each metal ion was transferred into five 250 mL Erlenmeyer flasks, corked and labeled. An accurately weighed sample of 1 g of each adsorbent was weighed into each of the flasks and agitated for time intervals of 10, 30, 60, 90 and 120 min, respectively. At the end of each agitation time (contact time), the content of each flask was filtered rapidly and filtrates collected into various sample bottles. The residual (equilibrium) concentration of the filtrate of each metal solution was analyzed using UNICAM 969 solar atomic absorption spectrophotometer (AAS).

### 3.1. Data Analysis

Experimental readings were carried out in triplicates and the average of each reading was used in the calculations. However, the amount of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  adsorbed ( $q_e$ ) from each metal solution at time,  $t$ , was computed using the equation shown below:

$$q_e = (c_o - c_e) v/m \quad (1)$$

where  $q_e$  is the amount of metal ion adsorbed at any given time,  $t$ , in mg/g;  $c_o$  is the initial metal ion concentration (mg/L);  $c_e$  is the metal ion concentration at equilibrium i.e. final concentration in solution (mg/L);  $v$  is the volume of initial metal ion solution used which is constant (50 mL);  $m$  is the mass of adsorbent used (i.e. 1 g).

## 4. Results and Discussion

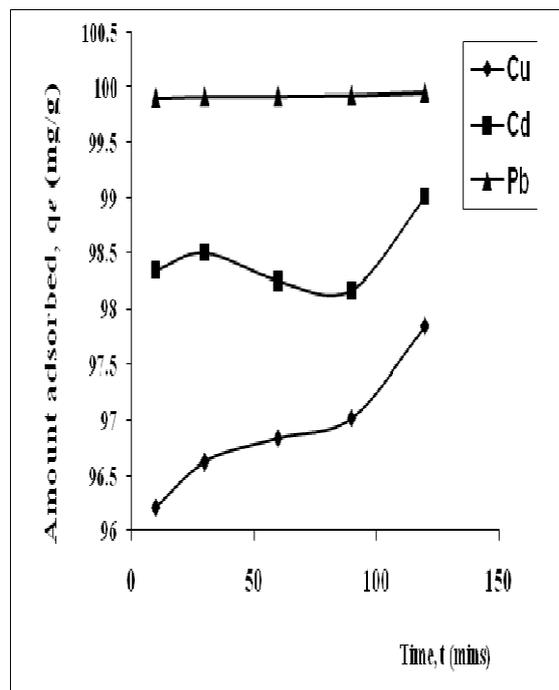
The treatment of the adsorbent with 2 % (v/v) dilute  $\text{HNO}_3$  solution (i.e. activation of the adsorbent) aids the removal of any debris or soluble biomolecules that might interact with metal ions during sorption. It also helps to open up the pores of the adsorbent in readiness for sorption reaction.

### 4.1. Effect of Contact Time on Sorption Capacity

The values for the amount of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  adsorbed by the unmodified breadfruit seed hull (UBSH) and modified breadfruit seed hull (MBSH) calculated through equation 1 above have been used to plot Figures 1 and 2 below.

Figure 1 shows the plot of amount adsorbed versus contact time for sorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  by the unmodified breadfruit seed hull (UBSH). From the figure, it could be seen that the amount of metal ions adsorbed increased with time. However, there was a slight drop in the amount of  $\text{Cd}^{2+}$  adsorbed at contact time 60 min and 90 min as well as an increase again at 120 min. The sorption trend for USBH was  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . Figure 2 shows the plot of amount adsorbed versus contact time for sorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  by the modified breadfruit seed hull (MBSH). From the plot, it could also be observed that the MBSH maintained fairly constant increase in the amount of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  adsorbed as the contact time

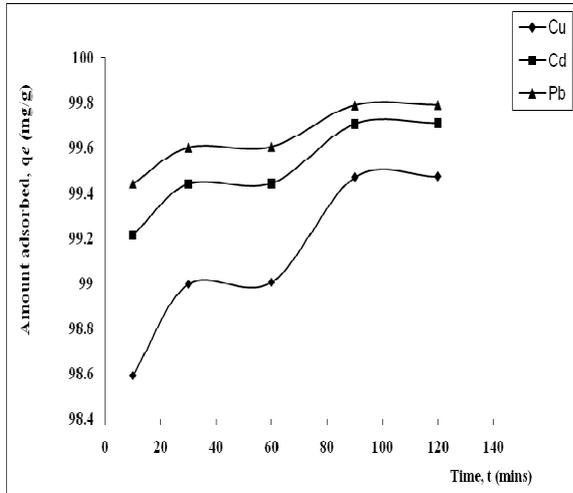
increased between 10 min and 120 min. The sorption trend was also  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ .



**Figure 1.** Variation of amount adsorbed,  $q_e$ , with contact time,  $t$ , for adsorption of  $\text{Cu}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Pb}(\text{II})$  ions onto Unmodified Breadfruit Seed Hull (MBSH).

Generally, appreciable uptake levels of the metal ions were achieved by the adsorbents (UBSH and MBSH) at the least contact time, 10 min. This means that the sorption process of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on USBH and MBSH was rapid and in 10 min, the process of adsorption nearly reached equilibrium. Thus, after 10 min contact time, the amount of adsorbed metal ions did not change very much or significantly with time. Hence, in the present sorption studies, 120 min was chosen as the equilibrium time. Other researchers have observed the same trend [27, 28]. Further examination on Figure 1 and 2 revealed that the amount of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  adsorbed by the modified adsorbent (MBSH) was higher than that of unmodified adsorbent (UBSH). The improved levels of the sorption of these metal ions ( $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) by the modified breadfruit seed hull is thought to result from the relative ease of exchanging hydrogen atoms of the  $-\text{SH}$  groups on thioglycollic acid with the heavy metal ions. Similar observations have been reported by other researchers [29, 30]. Conversely, thiolation of the breadfruit seed hull (MBSH) appears to reduce its sorption capacity for  $\text{Pb}^{2+}$  as shown in Figure 2. Thus, at 10 min contact time, the amount of  $\text{Pb}^{2+}$  adsorbed by MBSH was 49 % of the amount of  $\text{Pb}^{2+}$  adsorbed by USBH. This reduction in sorption capacity of modified breadfruit seed hull for  $\text{Pb}^{2+}$  may be due to an intrinsically low affinity of the  $\text{Pb}^{2+}$  for thiol ( $-\text{SH}$ ) groups. This is similar to the findings of previous studies [31, 32]. However, the discrepancy in the amounts of metal ions adsorbed can be explained in terms of the difference in the ionic size of the metal ions,

the nature and distribution of active or functional groups on the adsorbent and the mode of interaction between the metal ions and the adsorbent.



**Figure 2.** Variation of amount adsorbed,  $q_e$ , with contact time,  $t$ , for adsorption of  $\text{Cu}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Pb}(\text{II})$  ions onto Modified Breadfruit Seed Hull (MBSH).

### 4.2. Sorption Kinetics

The experimental results were modeled using Pseudo-first order and Pseudo-second order kinetic models as well as intraparticle diffusion models by Weber & Morris [33] and that of McKay & Poots [34]. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients ( $R^2$  values close or

equal to 1). A relatively high  $R^2$  value indicates that the model successfully describes the kinetics of the adsorption process.

Pseudo-first order model:

The pseudo-first order equation [35] is generally expressed as follows:

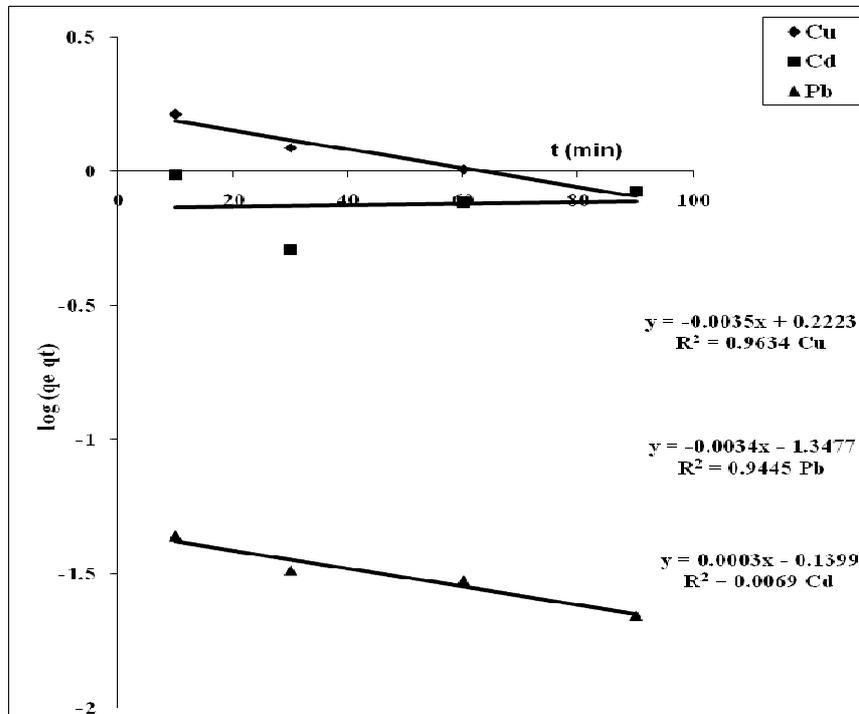
$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \tag{2}$$

where  $q_e$  and  $q_t$  are the adsorption capacities at equilibrium and at time,  $t$ , respectively,  $K_1$  is the rate constant of pseudo-first order adsorption ( $\text{min}^{-1}$ ).

After integration and applying boundary conditions,  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of equation (2) becomes:

$$\log (q_e - q_t) = \log (q_e) - \frac{K_1 t}{2.303} \tag{3}$$

The values of  $\log (q_e - q_t)$  were linearly correlated with  $t$ . The plot of  $\log (q_e - q_t)$  versus  $t$  for the metal ions using unmodified breadfruit seed hull (UBSH) is shown in Figure 3 while that of the modified breadfruit seed hull (MBSH) is shown in Figure 4. From these figures, the values of  $K_1$  and  $q_e$  were determined from the slope and intercept of the plots respectively. The linear regression equations and the correlation coefficients ( $R^2$ ) are shown on the figures. The kinetic parameters (constants) and  $R^2$  values for the pseudo-first order equation are presented in Table 1 below.



**Figure 3.** Pseudo-first order plot for adsorption of  $\text{Cu}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Pb}(\text{II})$  ions onto Unmodified Breadfruit Seed Hull(UBSH).

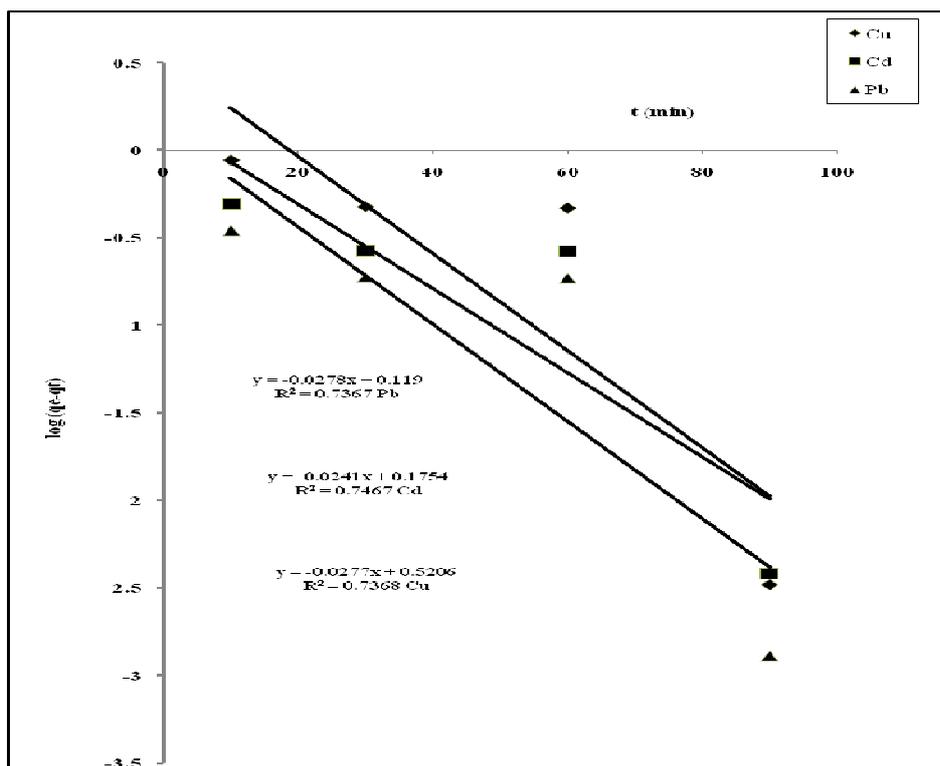


Figure 4. Pseudo-first order plot for adsorption of Cu (II), Cd (II) and Pb (II) ions onto Modified Breadfruit Seed Hull(MBSH).

As shown in Table 1, higher values of  $K_1$  were observed for MBSH than UBSH. The  $K_1$  values followed the trend  $Cu^{2+} > Pb^{2+} > Cd^{2+}$  for UBSH and  $Pb^{2+} > Cu^{2+} > Cd^{2+}$  for MBSH. However, the higher the  $K_1$  value, the greater the adsorption. On the other hand,  $q_e$  values showed the trend:  $Cu^{2+} > Cd^{2+} > Pb^{2+}$  for both UBSH and MBSH. Therefore, it indicates that the lower the  $q_e$  value, the greater the adsorption. In other words, the trend is  $Pb^{2+} < Cd^{2+} < Cu^{2+}$  for UBSH and MBSH, thus conforming to the adsorption capacity trend of the sorption process. Also from Table 1,  $R^2$  values close to 1 were obtained for  $Cu^{2+}$  and  $Pb^{2+}$  (excluding  $Cd^{2+}$ ) by UBSH, which indicates a good correlation, while  $R^2$  values by MBSH for all the metal ions were lower and not closer to 1, thereby giving poor correlation with Pseudo-first order equation. Generally, the obtained range of values for  $K_1$  and  $q_e$  as well as  $R^2$  values depict pseudo-first order equation as not a very good fit for the sorption process.

Table 1. Kinetic parameters and Correlation coefficients ( $R^2$  values) for Pseudo-first order model.

Constants (Units)	UBSH			MBSH		
	$Cu^{2+}$	$Cd^{2+}$	$Pb^{2+}$	$Cu^{2+}$	$Cd^{2+}$	$Pb^{2+}$
$K_1$ ( $min^{-1}$ )	0.00806	-0.000691	0.00783	0.0638	0.0555	0.0640
$q_e$ (mg/g)	1.6684	0.7246	0.0449	3.3159	1.4976	1.3152
$(R^2)$	0.9634	0.0069	0.9445	0.7368	0.7467	0.7367

Pseudo- Second order model:

The sorption data was also analyzed in terms of a pseudo-second order mechanism [36] using the equation below:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (4)$$

where  $K_2$  is the rate constant of pseudo-second order adsorption (g/mg-min). Integrating equation (4) and applying the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_1 t \quad (5)$$

Equation (5) is the integrated rate law for pseudo-second order reaction. Rearranging equation (5) gives a linear form as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

If the initial adsorption rate,  $h_0$  (mg/g- min) is

$$h_0 = K_2 q_e^2 \quad (7)$$

Then equations (6) and (7) will become

$$\frac{t}{qt} + \frac{1}{h_0} + \frac{t}{q_e} \quad (8)$$

The plot of  $t/q_t$  versus  $t$  for the metal ions using unmodified breadfruit seed hull (UBSH) is shown in Figure 5 while that of the modified breadfruit seed hull (MBSH) is shown in Figure 6. From the figures (5 & 6), the values of  $q_e$  and  $K_2$  were determined from the slope and intercept of

the plots, respectively. The plots gave a good fit to the experimental data. This means that the sorption process can be described by a pseudo-second order rate equation, hence  $q_e$ ,  $h_0$ ,  $K_2$  and  $R^2$  values were evaluated for the three metal

ions and for the UBSH and MBSH adsorbents respectively as presented in Table 2 below. The linear regression equations and the correlation coefficients ( $R^2$ ) are also shown on the figures.

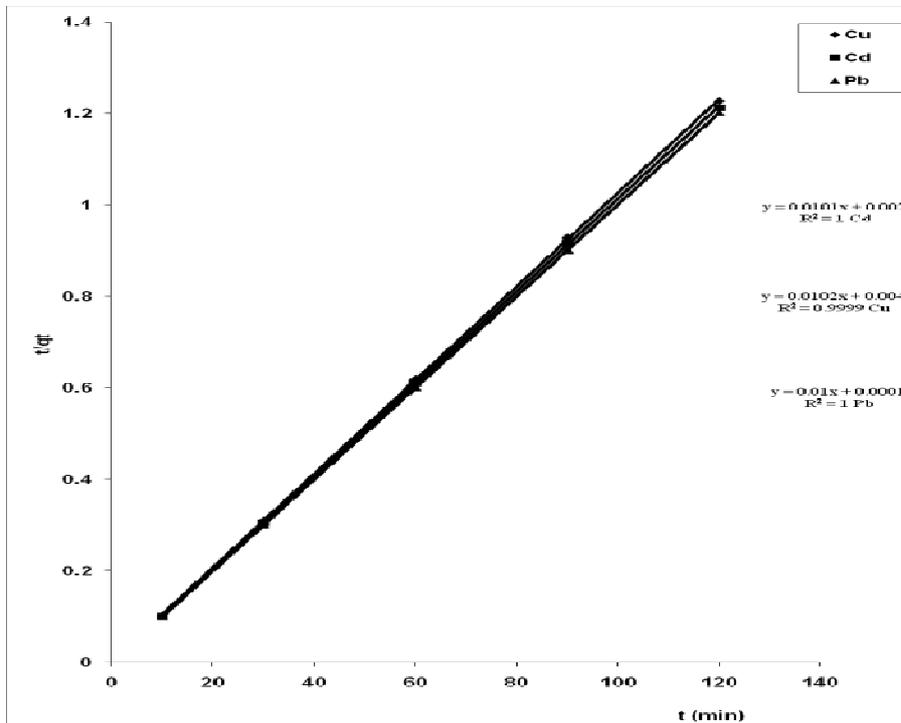


Figure 5. Pseudo-second order plot for adsorption of  $\text{Cu}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Pb}(\text{II})$  ions onto Unmodified Breadfruit Seed Hull(UBSH).

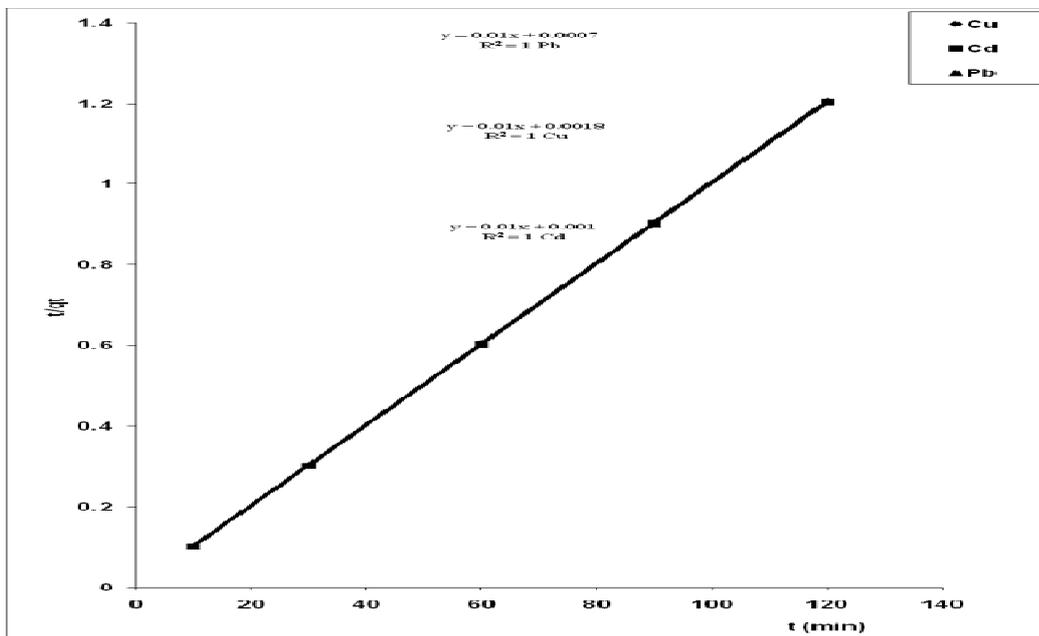


Figure 6. Pseudo-second order plot for adsorption of  $\text{Cu}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Pb}(\text{II})$  ions onto Modified Breadfruit Seed Hull(MBSH).

The results as presented in Table 2 showed that  $\text{Pb}^{2+}$  had the highest initial rate of sorption ( $h_0$ ) among the three metal ions for both UBSH and MBSH. Also  $K_2$  values were higher for  $\text{Pb}^{2+}$  than  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , considering the both adsorbents. The rate constant  $K_2$  gives a measure of how fast the reaction proceeds. The higher values of  $K_2$  for  $\text{Pb}^{2+}$

observed for both UBSH and MBSH are indications of higher reaction rates as well as higher adsorption rates for the sorption process. However, the trend of values of  $q_e$ ,  $h_0$  and  $K_2$  as shown in Table 2 is in direct conformity with the trend in adsorption capacity i.e.  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ .

Furthermore,  $R^2$  values from Table 2 are almost same for

all the three metal ions and the two adsorbents, with a value of 1, except for  $\text{Cu}^{2+}$  (0.9999) by UBSH. However, the obtained  $R^2$  value range of 0.9999 to 1 is clear indication that pseudo-second order model provided a better fit for the sorption process than the pseudo-first order model.

**Table 2.** Kinetic parameters and Correlation coefficients ( $R^2$  values) for Pseudo- second order model.

Constants (Units)	UBSH			MBSH		
	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$
$q_e$ (mg/g)	98.04	99.01	100.00	100.00	100.00	100.00
$h_0$ (mg/g-min)	250.00	500.00	10000.00	555.56	1000.00	1428.57
$K_2$ (g/mg-min)	0.0260	0.0510	1.0000	0.0556	0.1000	0.1429
$(R^2)$	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000

#### Intraparticle diffusion models

The mechanism of sorption is either film diffusion controlled or particle diffusion controlled [37]. Before adsorption takes place, several diffusion processes known to affect the adsorption process will take place. The adsorbate will have to diffuse through the bulk of the solution to the film surrounding the adsorbent and then into the micropores and macropores of the adsorbent. Several models have been developed for the studies of mechanism of sorp-

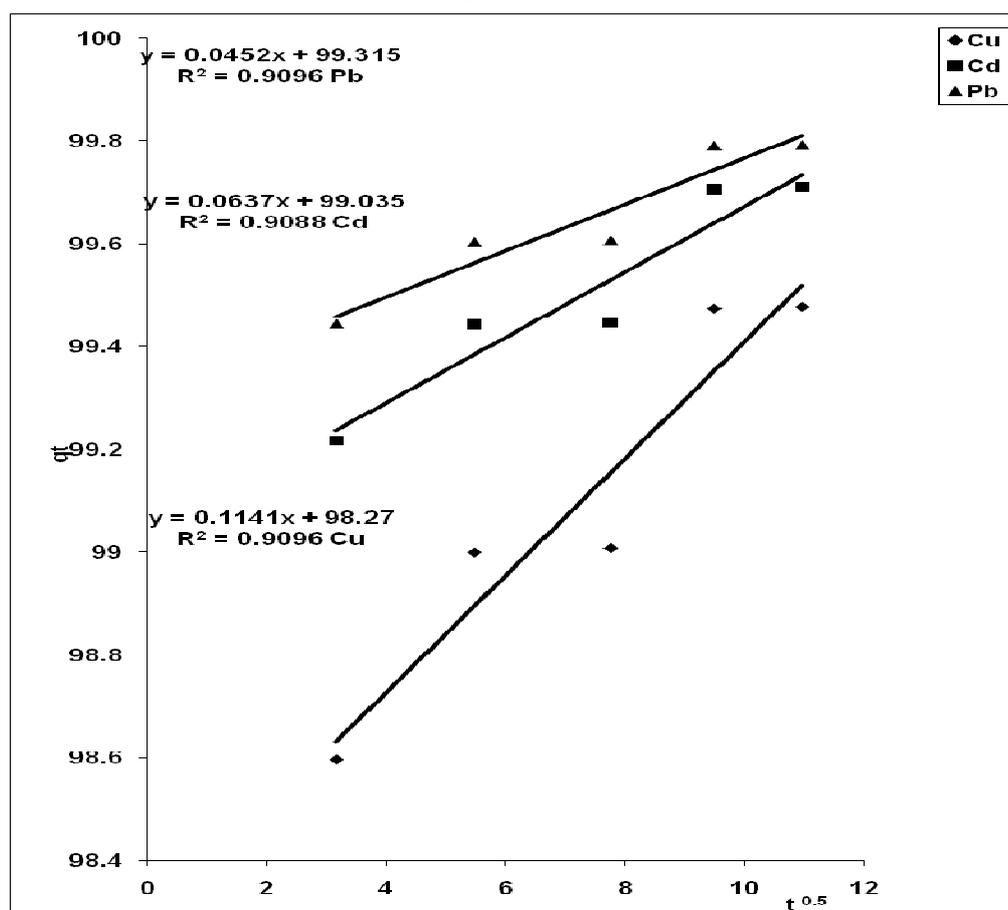
tion processes by intraparticle diffusivity. They include:

McKay & Poots model:

This model equation was developed by McKay and Poots [34]. They observed that the fraction of solute adsorbed can be expressed in terms of the square root of time as given in the equation:

$$q_t = X_i + K' t^{0.5} \quad (9)$$

where  $X_i$  is the boundary layer diffusion effects (mg/g),  $K'$  is the rate constant for intraparticle diffusion ( $\text{mg/g-min}^{-0.5}$ ). The plot of fraction of solute adsorbed  $q_t$  (i.e. amount adsorbed at each time, t) versus  $t^{0.5}$  (i.e square root of time) for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  by the unmodified adsorbent (UBSH) is shown in Figure 7 while that of the modified adsorbent (MBSH) is shown in Figure 8. The slope of the plots ( $q_t$  vs  $t^{0.5}$ ) gives the initial rate of sorption controlled by intraparticle diffusion,  $K'$  ( $\text{mg/g-min}^{-0.5}$ ) while the extrapolation of the linear plots to the time gives the intercepts of the plots,  $X_i$  (mg/g) which is proportional to the boundary layer thickness. The linear regression equations and the correlation coefficients ( $R^2$  values) are shown on the figures. The kinetic parameters as well as  $R^2$  values for McKay and Poots are presented in Table 3 below.



**Figure 8.** McKay & Poots Intraparticle diffusion plot for adsorption of  $\text{Cu(II)}$ ,  $\text{Cd(II)}$  and  $\text{Pb(II)}$  ions onto Modified Breadfruit Seed Hull(MBSH).

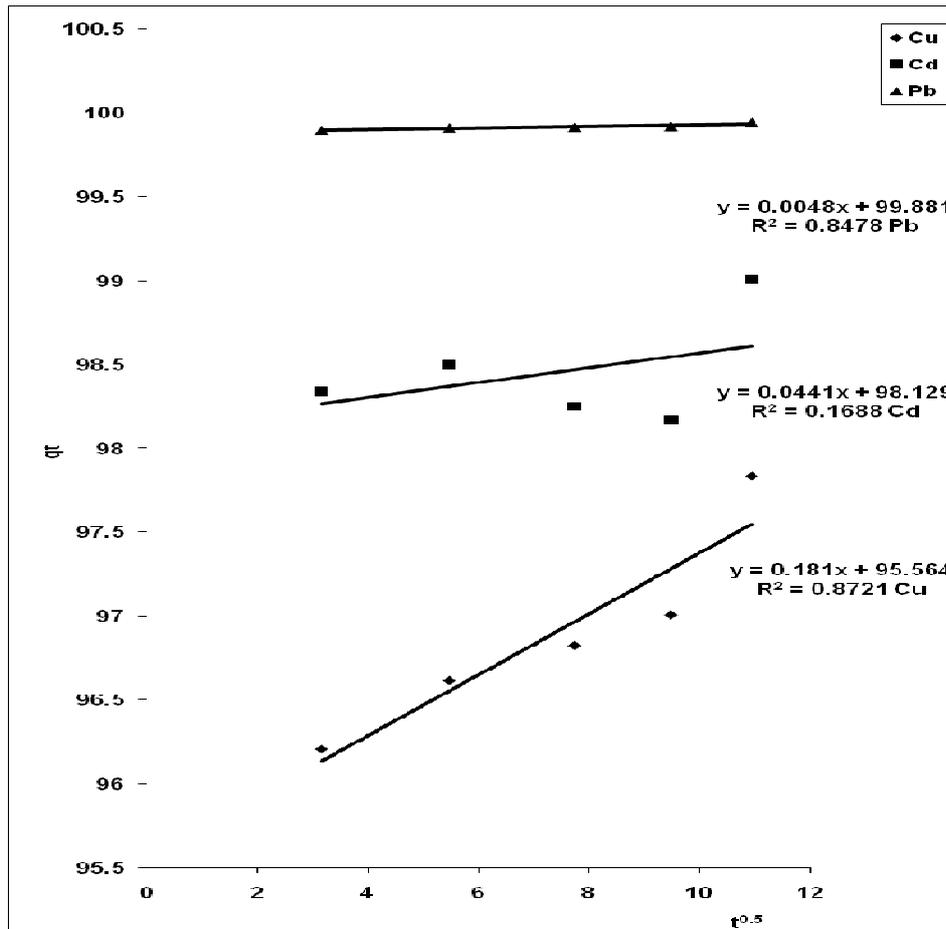


Figure 7. McKay & Poots Intraparticle diffusion plot for adsorption of Cu(II), Cd(II) and Pb(II) ions onto Unmodified Breadfruit Seed Hull(UBSH).

The results as presented in Table 3 showed that  $\text{Pb}^{2+}$  ions had highest  $X_i$  values than  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions for both UBSH and MBSH. However, higher values of  $X_i$  i.e. boundary layer thickness depict higher adsorption capacities. The boundary layer gives an insight into the tendency of the metal ions to adsorb to the adsorbent phase or remain in solution. Since diffusion takes place, the boundary layer is looked upon as a viscous drag existing between the adsorbent surface and the metal ion solution diffusing across its surface. Nonetheless, it has been reported that at a high temperature, the thickness of the boundary layer decreases due to the increased tendency of the metal ions to escape from the adsorbent surface to the solution phase, which results in a decrease in adsorption as the temperature increases [38, 32]. As shown in Table 3 below, the boundary layer thickness varied from 95.564 to 99.881 mg/g. This shows high tendency for adsorption capacity.

Table 3. Kinetic parameters and Correlation coefficients ( $R^2$  values) for McKay & Poots intraparticle diffusion model.

Constants (Units)	UBSH			MBSH		
	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$
$X_i$ (mg/g)	95.564	98.129	99.881	98.270	99.035	99.315
$K'$ (mg/g-min <sup>-0.5</sup> )	0.1810	0.0441	0.0048	0.1141	0.0637	0.0452
( $R^2$ )	0.8721	0.1688	0.8478	0.9096	0.9088	0.9096

The modified adsorbent (MBSH) has  $R^2$  values closer to 1 for all the metal ions investigated. However, the unmodified adsorbent (UBSH) showed appreciably higher  $R^2$  values for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  than  $\text{Cd}^{2+}$ . Generally, it could be said that the model fits the experimental data and also confirms that the sorption process is mainly intraparticle diffusion controlled, except in the sorption of  $\text{Cd}^{2+}$  by the UBSH where film diffusion is suspected due to low  $R^2$  value.

Weber & Morris Model:

Intraparticle diffusion model can also be expressed as [33, 39]:

$$R = K_{id}(t)^n \tag{10}$$

The logarithm of both sides of Equation 10 gives:

$$\log R = \log K_{id} + n \log (t) \tag{11}$$

where  $R$  is the per cent of metal ion adsorbed,  $t$  is the contact time (min),  $n$  is the gradient of linear plots and also depicts adsorption mechanism,  $K_{id}$  is the intraparticle diffusion rate constant ( $\text{min}^{-1}$ ) and may be taken as a rate factor, i.e. per cent metal ion adsorbed per unit time.

The plot of  $\log R$  versus  $\log t$  for the metal ions using unmodified adsorbent (UBSH) is shown in Figure 9 while that of the modified adsorbent (MBSH) is shown in Figure

10. From the plots,  $n$  (the gradient of the linear plots) and  $K_{id}$  (the intraparticle diffusion rate constant in  $\text{min}^{-1}$ ) gave the slope and intercept of the linear plots, respectively. The linear regression equations and the correlation coefficients ( $R^2$  value) are shown on the figures. The kinetic parameters,  $K_{id}$  and  $n$ , as well as  $R^2$  values for the model are presented in Table 4 below.

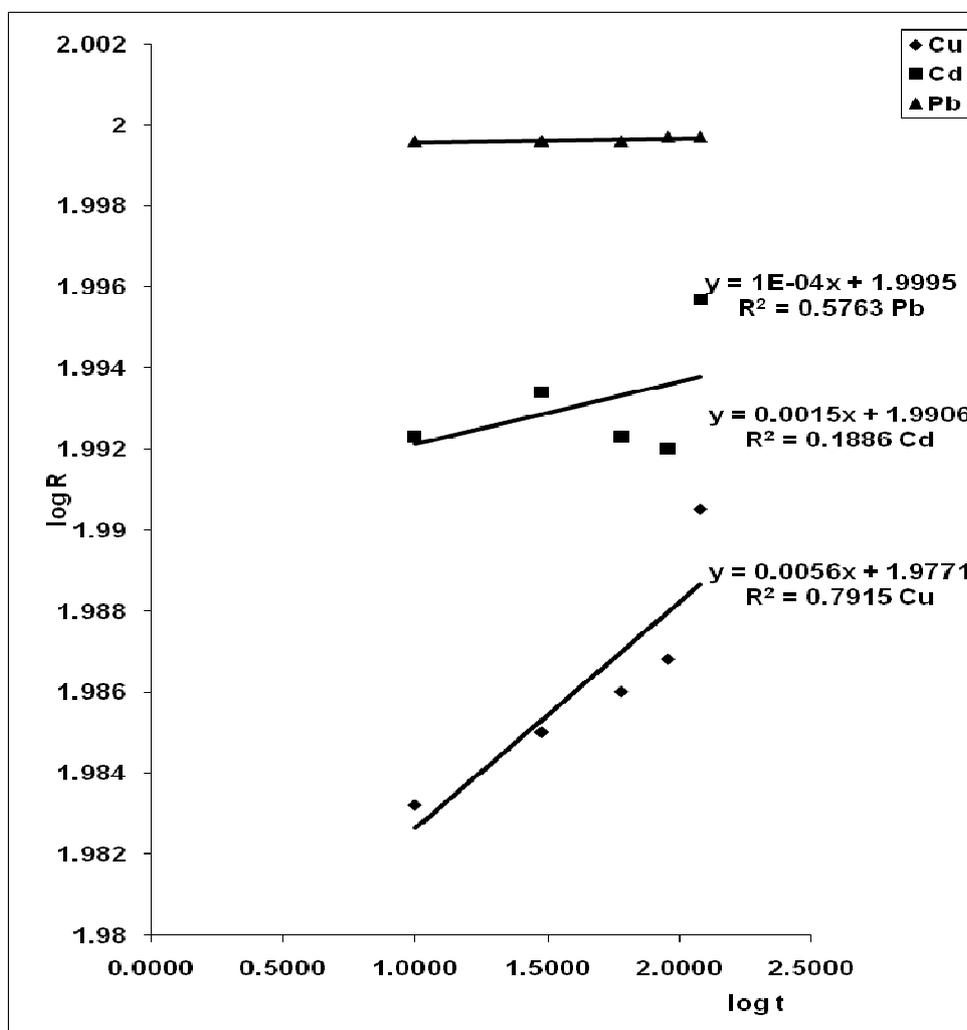
**Table 4.** Kinetic parameters and Correlation coefficients ( $R^2$  values) for Weber & Morris intraparticle diffusion model.

Constants (Units)	UBSH		MBSH			
	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$
$n$	0.005	0.0015	0.0001	0.0035	0.0019	0.0014
$K_{id}$ ( $\text{min}^{-1}$ )	94.864	97.859	99.885	97.791	98.764	99.129
( $R^2$ )	0.7915	0.1886	0.5763	0.9005	0.8976	0.8934.

The results presented in Table 4 showed that the  $K_{id}$  val-

ues increased in the order:  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$  for both UBSH and MBSH which is the same order as the adsorption capacity trend. However, higher values of  $K_{id}$  illustrate an enhancement in the rate of sorption while larger  $n$ -values illustrate a better adsorption mechanism which is related to an improved bonding between the metal ions and the adsorbent particles. From Table 4 also, the  $n$ -values increased in the order  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$  for both UBSH and MBSH, which is in the reverse order of adsorption capacity trend. The obtained  $K_{id}$  and  $n$ -values therefore signify that the sorption process is particle diffusion controlled and that the intraparticle mass transfer resistance is the rate-limiting step [40, 41, 30]. However,  $R^2$  values obtained showed higher values for MBSH than UBSH with Weber & Morris model.

Generally, in terms of intraparticle diffusion, the sorption process was found to be intraparticle diffusion controlled, with MBSH fitting the McKay & Poots model better than Weber & Morris model.



**Figure 9.** Weber & Morris Intraparticle diffusion plot for adsorption of Cu(II), Cd(II) and Pb(II) ions onto Unmodified Breadfruit Seed Hull(UBSH).

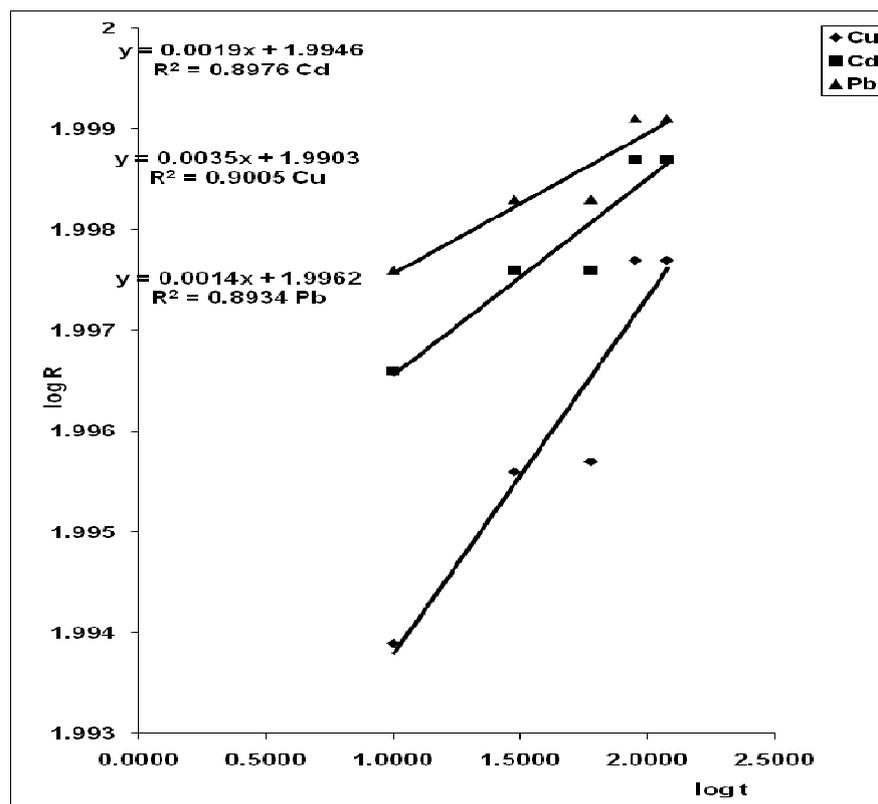


Figure 10. Weber & Morris Intraparticle diffusion plot for adsorption of  $\text{Cu}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Pb}(\text{II})$  ions onto Modified Breadfruit Seed Hull (MBSH).

## 6. Conclusion

The laboratory-scale experiments carried out have shown that African breadfruit (*Treculia africana*) seed hull is a good adsorbent for the removal of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solutions. Sorption capacity for the metal ions was in the order:  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$  by both UBSH and MBSH. Modification of the adsorbent by thiolation enhanced its sorption capacity. The sorption process was found to follow Pseudo-second order kinetics. Among the two intraparticle diffusion models tested, McKay & Poots model gave a better fit than Weber & Morris model.

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