

# Intraparticle and Liquid film Diffusion Studies on the Adsorption of $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ Ions from Aqueous Solution using Powdered Cocoa Pod (*Theobroma cacao*)

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**Abstract**-The ability of powdered cocoa pod to adsorb ( $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ) from aqueous solutions was investigated. The adsorption technique was carried out using five different particle sizes (75  $\mu\text{m}$ , 300  $\mu\text{m}$ , 600  $\mu\text{m}$ , 850  $\mu\text{m}$ , and 1200  $\mu\text{m}$ ) of the cocoa pod and 60 mg/L of synthetic solutions containing the metal ions. The supernatants obtained after the adsorption process were analyzed to determine the residual metal ions using Atomic Absorption Spectrophotometer (GBC Avanta Ver.2.02/Analysis 1anl.). The study shows that the smallest particle size (75  $\mu\text{m}$ ) achieved the highest percent adsorption of 89.5 - 91% and 97.3 - 98.5% for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions respectively. The regression coefficient ( $R^2$ ) values for the liquid film diffusion plots for  $\text{Cu}^{2+}$  (0.9735) and  $\text{Pb}^{2+}$  (0.9115) were quite high showing the relevance of film diffusion as a rate determining factor in the adsorption process. Furthermore, the liquid film diffusion rate constant ( $K_{fd}$ ) values show that  $\text{Cu}^{2+}$  (0.0016) adsorption was slower than  $\text{Pb}^{2+}$  (0.018). The Intraparticle diffusion constant ( $k_{id}$ ) values for the macropore and micropore diffusion stages for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions show that the rate limiting step was the micropore diffusion stage. This is because the micropore diffusion constant  $k_{id2}$  values for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions (0) was lower than those for the macropore diffusion constants  $k_{id1}$  of 0.023 for  $\text{Cu}^{2+}$  and 0.284 for  $\text{Pb}^{2+}$  ions.

Keywords: Intraparticle, film Diffusion, Adsorption, Aqueous Solution, Cocoa pod.

## 1. INTRODUCTION

Heavy metals are very toxic and pose a threat to man and the environment, high concentration of heavy metals in the environment can be detrimental to a variety of living species [1]. Living organisms require trace amount of some of these heavy metals including Iron, cobalt, copper, manganese, molybdenum, vanadium, strontium and zinc but excessive levels can be detrimental to the organisms [2]. Whereas, other heavy metals such as mercury, lead and cadmium have no known vital beneficial effect on living organisms, their accumulation in the environment causes serious environmental and ecosystem imbalance, hence, results to different kinds of adverse health conditions [1, 3]. Therefore, the elimination of heavy metals from the environment is important as a result of their high toxicity, and at least to protect public health [4, 5].

Agro-wastes used as raw materials for the removal of toxic and precious metals from wastewater have continued to attract attention among researchers. This is because these materials are not only cheap but also simple, sludge-free, environmental - friendly, and the technique involves small initial cost. This has led many researchers to look for several

agricultural by-products and unused abundant plant species for the preparation of adsorbents. The sorption of heavy metal pollutants using agricultural by-products is an innovative method which has attracted a lot of attention in years past to control and detoxify heavy metal pollutants. The use of some agricultural by-products for the remediation of solutions containing heavy metals have been reported; maize cob and husk [6], sawdust [7, 8, 9, 10], Cassava waste [11], cocoa pod husk [12] and for the removal of dyes using water spinach [13].

The objective of this study is therefore to investigate the potential ability of powdered cocoa pod as an adsorbent for the removal of metal ions from aqueous systems, and to determine the suitability of intraparticle diffusion and liquid film diffusion models for the adsorption process.

## 2. MATERIALS AND METHODS

The cocoa pods (*Theobroma cacao*) were collected from Amassoma forest in Wilberforce Island of Southern Ijaw Local Government Area of Bayelsa state, Nigeria. The samples were washed thoroughly with water, rinsed with distilled water and sun-dried. The sun-dried cocoa pods were then cut into small pieces and ground into fine particles using a grinder. The ground sample was taken to the Department of Civil Engineering Laboratory, Niger Delta University, and sieved to obtain; 75  $\mu\text{m}$ , 300  $\mu\text{m}$ , 600  $\mu\text{m}$ , 850  $\mu\text{m}$  and 1200  $\mu\text{m}$  sizes.

### 2.1 Metal Ions Studied

The metal ions ( $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ) being studied were salts of  $\text{CuSO}_4$  and  $\text{Pb}(\text{NO}_3)_2$  respectively, and these salts were manufactured by Poole, BH15 LTD, England.

### 2.2 Preparation of Stock Solutions

Stock solutions of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions were prepared from the salts  $\text{CuSO}_4$  and  $\text{Pb}(\text{NO}_3)_2$  respectively. For  $\text{Cu}^{2+}$  ions, 1000 mg/L stock solution was prepared by dissolving 2.51g of  $\text{CuSO}_4$  in 1000ml volumetric flask and made up to the calibration mark.

While 1000 mg/L stock solution of  $\text{Pb}^{2+}$  was prepared by dissolving 1.60g of  $\text{Pb}(\text{NO}_3)_2$  in a 1000 ml volumetric flask and made up to the calibration mark. For the various experiments, serial dilutions were made from the above stock solutions using distilled water.

### 2.3 Determination of the effect of contact time

Into five (5) separate 250 ml conical flasks was introduced 1g each of powdered cocoa pod of 75  $\mu\text{m}$  mesh size. 50 ml of  $\text{Cu}^{2+}$  solution with concentration of 60 mg/L, prepared from the stock solution, was then transferred into each of the conical flasks. The flasks were labelled for time intervals of 20, 40, 60, 80 and 100 minutes. The flasks were then placed on a mechanical shaker and agitated at 150 rpm for the appropriate time interval. The suspensions were filtered through Whatmann filter papers at the end of agitation time. The filtrate was then analyzed using Atomic Absorption spectrophotometer (GBC Avanta Ver.2.02/Analysis 1anl.). This experiment was repeated using  $\text{Pb}^{2+}$  ion solution.

### 2.4 Effect of Particle Size

Into five (5) separate 250 ml conical flasks were introduced 1g of powdered cocoa pod of particle size 75, 300, 600, 850, and 1200 $\mu\text{m}$  respectively.

50 ml each of solution containing 60 mg/L of  $\text{Cu}^{2+}$  was transferred into the conical flasks containing the various particle sizes. The conical flasks were then placed on a mechanical shaker and agitated at 150rpm for 80 minutes. At the end of 80 minutes, the solutions were filtered with Whatmann filter paper and the filtrate analyzed for residual metal ions using AAS. The experiment was then repeated using  $\text{Pb}^{2+}$  ion solution.

## 2.5 ANALYSIS OF EXPERIMENTAL DATA

The equilibrium sorption capacity of the cocoa pod at a given time was determined by using the mass balance equation (1)

$$q_t = V/m (C_o - C_e) \quad (1)$$

Where  $q_t$  is the amount of metal ions adsorbed onto the pod ( $\text{mg g}^{-1}$ ) at time  $t$ ,  $C_o$  is the initial metal ion concentration ( $\text{mg L}^{-1}$ ),  $C_e$  is the equilibrium metal ion concentration ( $\text{mg L}^{-1}$ ), and  $V$  is the volume of the medium (L) and  $m$  is the mass of pod used in the adsorption process (g).

To investigate if intra-particle diffusion was the sorption rate limiting step, the Weber-Morris plot of  $q_t$  versus  $t^{1/2}$  was taken (2)

$$q_t = K_{id}t^{1/2} + C \quad (2)$$

Where  $K_{id}$  is the intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) and  $C$  ( $\text{mg g}^{-1}$ ) is a constant that gives an idea about the thickness of the boundary layer; it was observed that the larger the value of  $C$  the greater the boundary layer effect [14]. If the Weber-Morris plot of  $q_t$  versus  $t^{1/2}$  gives a straight line, then the sorption process was controlled by intra-particle diffusion only and the slope gives the rate constant,  $K_{id}$ . However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process.

Liquid film diffusion model was also used in this study to investigate if transport of metal ions from the liquid phase up to the solid phase boundary also plays a role in the adsorption process equation (3)

$$\ln (1-F) = -K_{fd}t \quad (3)$$

where  $F$  is the fractional attainment of equilibrium ( $F = q_t/q_e$ ),  $K_{fd}$  is liquid film diffusion constant. A linear plot of  $-\ln (1-F)$  versus  $t$  with zero intercept would suggest that the kinetics of the sorption process was controlled by diffusion through the liquid surrounding the solid sorbent.  $q_e$  is the adsorption capacity of the sorbent at equilibrium ( $\text{mg g}^{-1}$ )

## 3. RESULTS AND DISCUSSION

The effect of particle size of powdered cocoa pod on the percent removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions from aqueous solution is presented in figure 1, and it shows that as the particle size increases, the concentration of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in solution at equilibrium also increased. This shows that as the particle size increased the amount of metal ions removed decreased and as the particle size decreases, the percentage of metal ions removed from solution increased.

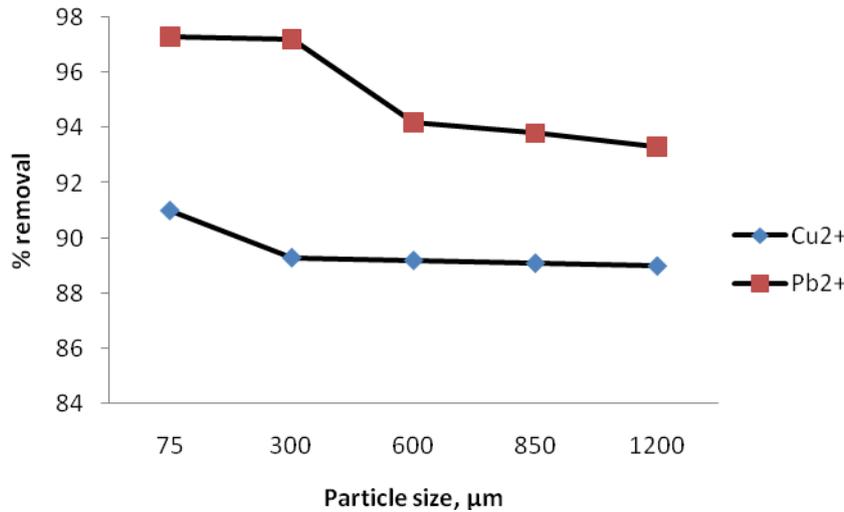


Fig 1: Effect of particle size on the percent removal of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions

This was not unexpected because the smaller the particle size, the larger the surface area and the higher the adsorption capacity. It has been established that the larger the surface area of an adsorbent, the higher the percent adsorption. The plots in figure 1 further shows that for the same particle size, the percent of Pb<sup>2+</sup> ions adsorbed from solution was higher than that for Cu<sup>2+</sup> ions.

The effect of time on the percent removal of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions from aqueous solution by powdered cocoa pod was also studied and presented in figure 2. It shows that the percent removal of both Cu<sup>2+</sup> and Pb<sup>2+</sup> ions increased with time. The highest percent removal of both metal ions occurred at 80 mins; beyond 80 mins, the percent removal decreased slightly both for Cu<sup>2+</sup> and Pb<sup>2+</sup> ions. This shows that before 80 minutes contact time, the adsorbent surface was not completely covered with metal ions and there were vacant spaces that needed to be occupied.

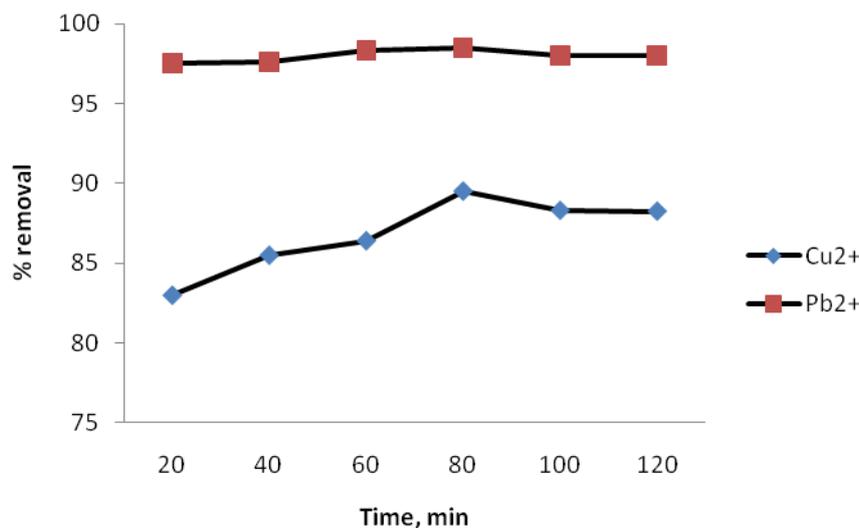


Fig 2: Effect of time on the percent removal of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions

At 80 minutes, the entire adsorbent surface seems to have been fully occupied by metal ions. And beyond 80 minutes, desorption may have occurred due to repulsion between like charges on the fully occupied surface of the adsorbent. Figure 2 also reveals that the percent removal of  $Pb^{2+}$  ions was higher than that of  $Cu^{2+}$  ions. Going by the observed order of adsorption of the metal ions in Figures 1 and 2 ( $Pb > Cu$ ), it may be deduced that the anions of the metal salts played significant contributory roles in the extent of adsorption. If ionic size is to rank first in the above mentioned determinants, then the capacity of  $Cu^{2+}$  ion ( $0.73 \text{ \AA}$ ) should be greater than  $Pb^{2+}$  ( $1.20 \text{ \AA}$ ) by reason of its smaller ionic size. However, the percent adsorption of  $Pb^{2+}$  was higher than for  $Cu^{2+}$ . This order may be due to the increasing basic strength of the anions;  $NO_3^- > SO_4^{2-}$ . This observation is consistent with other findings [15]. The anion of  $Cu^{2+}$ ,  $SO_4^{2-}$  is the weaker Lewis base among the two anions, therefore a chemisorption process will proceed slower in  $CuSO_4$  than for  $Pb(NO_3)_2$ . The  $SO_4^{2-}$  ion has a higher tendency to remain in solution with its cation than the  $NO_3^-$  ion.

The time dependent data from this study was further used to investigate whether intra-particle and liquid film diffusion kinetics also played significant roles in the adsorption of  $Cu^{2+}$  and  $Pb^{2+}$  ions from their aqueous solutions. The intra-particle diffusion kinetic plots of  $q_t$  against  $t^{1/2}$  for  $Cu^{2+}$  and  $Pb^{2+}$  were taken and presented in figures 3 and 4 respectively.

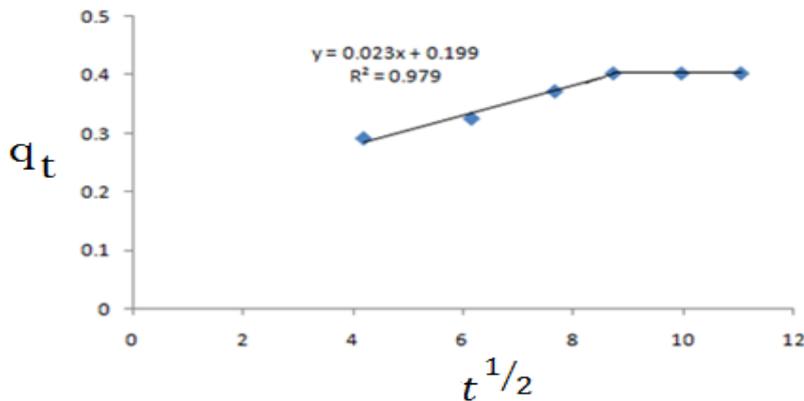


Fig 3: Intraparticle diffusion plot for the removal of  $Cu^{2+}$  ion from aqueous solution

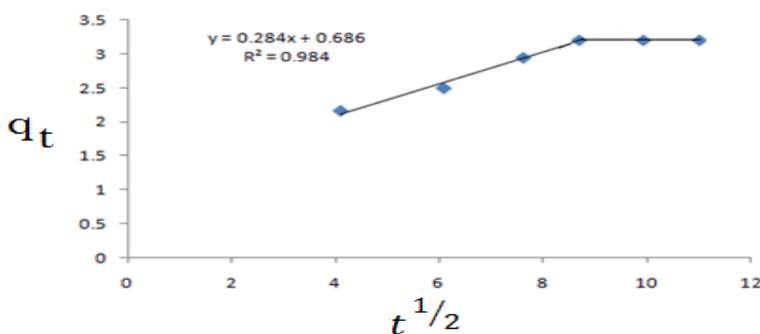


Fig 4: Intraparticle diffusion plot for the removal of  $Pb^{2+}$  ion from aqueous solution

The intra-particle diffusion constants obtained from the slopes and intercepts of figures 3 and 4 and their regression coefficients ( $R^2$ ) for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions are presented in table 4.

**Table 4:** Intra-particle and liquid film diffusion constants and regression coefficients ( $R^2$ ) for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions.

	Intra-particle Diffusion						Liquid film Diffusion		
	$K_{id1}$	Intercept	$R_1^2$	$K_{id2}$	Intercept	$R_2^2$	$K_{fd}$	Intercept	$R_f^2$
$\text{Cu}^{2+}$	0.023	0.199	0.979	0	0.41	NA	0.0016	0.0791	0.9735
$\text{Pb}^{2+}$	0.284	0.686	0.984	0	3.20	NA	0.018	0.778	0.9115

NA = Not available

Comparing the  $k_{id}$  values for the macropore and micropore diffusion stages for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions show that the rate limiting step is the micropore diffusion stage. This is because the micropore diffusion constant  $k_{id2}$  values for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions were both zero (0); lower than those for the macropore diffusion constants  $k_{id1}$  of 0.023 and 0.284 respectively for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions. This shows that the rate of micropore diffusion is the slower step and the rate determining step. The boundary layer effect i.e. the intercepts of the second lines from the plots in figures 3 and 4 were also presented in table 4 which further shows greater effect at the micropore diffusion stage (0.41 and 3.20) respectively for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions than at the macropore stage (0.199 and 0.686) for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions respectively.

The liquid film diffusion model plots of  $-\ln(1-F)$  versus time were also taken for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions and presented in figure 5. From the intercepts and slopes of figure 5, the film diffusion parameters were obtained and given in table 4. The intercept values for both  $\text{Cu}^{2+}$  (0.0791) and  $\text{Pb}^{2+}$  (0.778) are higher than zero, but are close to the origin showing the significance of liquid film diffusion in the rate determination of the adsorption process [14].

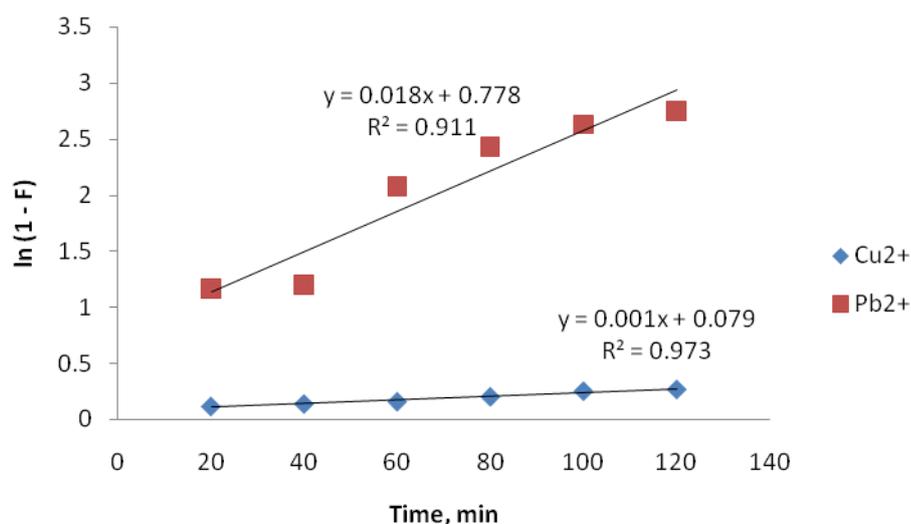


Fig 5: Liquid film diffusion model plots for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions from aqueous solution

The regression coefficient ( $R^2$ ) values for  $\text{Cu}^{2+}$  (0.9735) and  $\text{Pb}^{2+}$  (0.9115) were quite high showing the relevance of film diffusion as a rate determining factor in the adsorption process. Furthermore, the liquid film diffusion rate constant ( $K_{fd}$ ) values show that  $\text{Cu}^{2+}$  (0.0016) adsorption was slower than  $\text{Pb}^{2+}$  (0.018) adsorption.

#### 4. CONCLUSIONS

The result showed that powdered cocoa pod is a novel agricultural material for the removal of metal ions from their aqueous solutions. It was found that the smaller the particle size of the waste pod the higher the amount of metal ion removed from solution. The percent removal of  $\text{Pb}^{2+}$  ion was higher than that of  $\text{Cu}^{2+}$  which may be due to the type of anion attached to the metal ion. There was significant evidence to show that liquid film diffusion was also a rate determining step in the adsorption process. The regression coefficient ( $R^2$ ) values for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  were quite high showing the relevance of film diffusion as a rate determining factor in the adsorption process. Furthermore, the liquid film diffusion rate constant ( $K_{fd}$ ) values show that  $\text{Cu}^{2+}$  adsorption was slower than  $\text{Pb}^{2+}$ . The  $k_{id}$  values for the macropore and micropore diffusion stages for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions show that the rate limiting step is the micropore diffusion stage.

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