

Kinetics and Mechanisms of Sorption of Lead (II) Ions Using Carbonized and Mercapto-Acetic Acid Modified Sorghum (*Sorghum Bicolor*) Hull of Two Pore Sizes

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Abstract—Aim of this study was to investigate the use of carbonised and modified Sorghum hull in the removal of Lead metal ions from aqueous solution. The effect of contact time was investigated and reported. The maximum adsorption time for 150 μ m and 250 μ m were at the 40th and 80th minutes respectively (32.581mg/l and 39.309). The smaller particle size of 150 μ m mesh showed faster adsorption rate than particle size of 250 μ m mesh. Kinetic modelling of the results were also investigated. These results showed that Pseudo second order kinetic model best describe the process and the Mechanism of adsorption indicated that it was film diffusion controlled. This will serve as parameters to consider in the design of treatment plants for heavy metal detoxification using biosorbents.

Keywords—Biosorbents, detoxification, heavy metals, ADORPTION KINETICS, SORPTION MECHANISMS, pore size, thiolation, biosorption.

INTRODUCTION

Recent environmental concerns as well as heightened defence against chemical terrorism call for both new protection technologies and for the improvement of existing ones including adsorption. Adsorption, an established industrial separation technique used in bulk separation technique used both in bulk/batch separation and purification suited for the solution of such problems. Current challenges call for more new efficient and selective adsorbents. To accomplish these needs, new direction point to the development of adsorbents of a combined and hybrid nature such as organic and inorganic material made, carbon and combined adsorbents, regulation of lingo-cellulosic materials sorption properties by modification for environmental application.

Biosorption consists of a group of applications which involve the detoxification of hazardous substances instead of transferring them from one medium to another by means of microbes and plants. This process is characterised as less disruptive and can be often carried out on site eliminating the costly need to transport the toxic materials to treatment sites (IMAGA and Abia, 2014), biosorbents are prepared from naturally abundant and/or waste biomass. Due to

high uptake capacity and very cost-effective source of the raw material, biosorption is a progression towards a perspective method. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown levels of high enough to warrant further research. Biosorbent of plant origin are mainly agricultural by-products such as Sugar beet pulp (Zolgharnein *et al.*, 2011), Maize wrapper (Babarinde *et al.*, 2008), Maize cob (Opeolu *et al.*, 2009), modified Saw dust of Spruce (Urik *et al.*, 2009).

HEAVY metal refers to any chemical element with a specific gravity that is at least five times the specific gravity of water and is toxic or poisonous at higher amounts (Horsfall 2011)

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

Lead is a chemical element in the carbon group with symbol Pb and atomic number 82. It is a soft, malleable and heavy post-transition metal. Metallic lead has a bluish-white colour after being freshly cut, but it soon tarnishes to a dull grayish colour when exposed to air. Lead has a shiny-chrome-silver lustre when it is melted into a liquid. It is also the heaviest non-radioactive element. Lead is used in building construction, lead-acid batteries, bullets and shot, weights, as part of solders, pewters, fusible alloys and as a radiation shield. If ingested, lead is poisonous to animals and humans, damaging the nervous system and causing brain disorders. Excessive lead also causes blood disorders in mammals. Lead is a neurotoxin that accumulates both in soft tissues and the bones.

Sorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate at the solid-liquid interface. Studies on the kinetics of metal sorption by various adsorbents are of importance for designing an adsorption system. The rate at which sorption takes place is of utmost importance when designing batch sorption systems. Consequently it is important to establish the time dependence of such systems for various processes (Imaga C. *et al.*, 2014). The results from such studies

provide information on the minimum time required for considerable adsorption to take place and information on diffusion control mechanism between metal ions as they move towards the adsorbent surface.

In this study, a lingo-cellulosic material (Sorghum Hull) was used as biosorbent in the removal of heavy metal (Lead (II) ion) from aqueous solution in a batch sorption system. The effects of contact time, sorption kinetics and mechanisms of the carbonised and Mercapto-acetic acid modification and Particle size will be investigated.

MATERIALS AND METHODS

The Sorghum Hulls (*Sorghum bicolor*) were sourced from a brewery (Consolidated Breweries plc, Imo State, Nigeria). The material Sorghum Hull was later abbreviated as 'SH'. All reagents used were analytical grades purchased and used without further purification.

METHODS

(1) ADSORBENT PREPARATION

The Sorghum Hulls were washed and air dried in preparation for the adsorption analysis. The air dried Sorghum Hulls were crushed with a manual blender to smaller particles and sieve analysis was performed using the mechanical sieve screen to obtain final sample sizes of 150 μ m and 250 μ m.

(2) ACTIVATION OF SORGHUM HULLS

The screened fine Sorghum Hulls powder was further soaked in excess of 3.0M HNO₃ solution for 24 hours. It was then filtered through a Whatman No.41 Filter paper and rinsed with deionised water.

The rinsed Sorghum Hulls were later air dried for 24 hours. The treatment of the biomass with 3.0M HNO₃ solution aids the removal of any debris or soluble biomolecules that might interact with metal ions during sorption. This process is called chemical activation of the Sorghum Hulls.

(3) CARBONISATION OF THE SORGHUM HULLS:

The process was carried out using a Muffle furnace (Carbolite Sheffield, England, LMF4) which allowed limited supply of air. The carbonization took place at 250°C for one hour after which the charred products were allowed to cool to room temperature.

(4) CHEMICAL MODIFICATION OF SORGHUM HULLS WITH MERCAPTO-ACETIC ACID (MAA)

The air-dried activated and carbonated Sorghum Hulls were acid treated by dissolving it in excess 1.0M Mercapto acetic acid (HSCH₂COOH) solution, stirred for 30 minutes and left to stand for 24 hours at 28°C and was called Carbonised and Modified Sorghum Hull abbreviated as CMSH 150 μ m and 250 μ m.

After 24 hours, the mixtures in the beakers designated as CMSH 150 μ m and 250 μ m were filtered off using Whatman No. 41 filter paper and were air dried. The two working adsorbents were stored in air tight plastic containers and labelled respectively.

(5) PREPARATION OF ADSORBATE SOLUTIONS FOR SORPTION STUDIES

A stock solution of 1000ppm of the metal Lead was prepared from Lead (II) Nitrate (V) (M and B laboratory reagent, 98% assay). Thereafter, serial dilution was carried out on the stock solution to obtain working solution of 60 ppm of the metal ion. The concentration of the standard was confirmed using an Atomic Adsorption Spectrophotometer. The pH of the solution was kept at 7.0.

(6) SORPTION STUDIES AT DIFFERENT CONTACT TIME

Kinetics of sorption studies were carried out according to the method described by Imaga C. *et al.*, 2014. Kinetics of sorption for Pb²⁺ was carried out for each adsorbent (CMSH 150 μ m and 250 μ m) at pH of 7.0 and temperature of 28°C(301K). 30cm³ of standard solution of the metal, initial concentration of 60mg/l was transferred into various 250cm³ Erlenmeyer flask and labelled. Then 0.2g of each adsorbent CMSH 150 μ m and 250 μ m was transferred into the different flasks and agitated in a shaker for different contact times (20, 40, 60, 80 and 100 minutes). After each agitation time, the content of the flask was then filtered using Whatman No.41 filter paper. The residual concentration of metal ions in 20cm³ of the filtrate of each metal solution was determined using Atomic Adsorption Spectrophotometer (AAS) (GBC SCIENTIFIC AVANTA PM AAS A.C.N 005472686 manufactured by GBC Scientific equipment Pty Ltd. Dandenong Victoria Australia.). The adsorbed concentration was then calculated by difference. Glass wares and plastic wares were washed with deionized water and rinsed to eliminate errors (Imaga C. *et al.*, 2014).

RESULTS AND DISCUSSION

a) EFFECT OF CONTACT TIME ON AMOUNT OF METAL ION ADSORBED

The amount of metal adsorbed by an adsorbent at a particular time is one of the factors governing the efficiency of adsorption. The amount of Pb²⁺ adsorbed by the adsorbents CMSH 150 μ m and 250 μ m as a function of time is presented in table 1. The variation in the amount of the metal ion adsorbed by the adsorbents is shown in figure 1.

TABLE 1: EFFECT OF CONTACT TIME ON AMOUNT OF METAL ION CONCENTRATION ADSORBED FOR CMSH 150 μ m AND 250 μ m

CONTACT TIME(MINS)	AMOUNT OF METAL ION CONCENTRATION ADSORBED	
	Pb ²⁺ 150 μ m	Pb ²⁺ 250 μ m
20	29.589	37.029
40	32.581	36.781
60	30.234	38.735
80	29.536	39.309
100	30.562	37.462

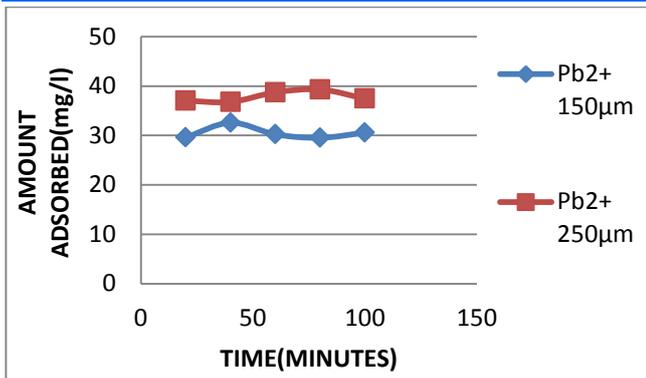


FIG 1: Graph of Amount Adsorbed versus Contact Time for Pb²⁺ (CMSh 150µm and 250µm)

The rate of adsorption in 150µm occurred faster (40th minute) than in 250µm (80th minute). This could be attributed to the pore size of the adsorbent, in that smaller pore sizes gives faster rate of adsorption while larger pore sizes gives slower rate of adsorption. The smaller pore size (150µm) has larger surface area than the 250µm which has a smaller surface area. The slower rate of reaction of 250µm resulted in the adsorbent adsorbing more of the metal ion (39.309mg/l) than 150µm (32.581mg/l) whose rate was faster.

(b) KINETIC MODELLING:

Quantification of the changes in sorption of metals with time requires the use of appropriate kinetic model. The kinetic models Pseudo first and Second order and Elovich models were employed to investigate the kinetics of sorption of the divalent metal ion by the adsorbents.

(I) PSEUDO-FIRST ORDER MODEL

The pseudo-first order adsorption kinetic rate equation is expressed as:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad [1]$$

Where,

q_e is the equilibrium biosorption capacity in mg/g

q_t is the sorption capacity at any time, t in mg/g

K_1 is the pseudo-first order rate constant in $\text{mg}^{-1} \cdot \text{min}^{-1}$

The plot of the pseudo- first order is not shown as the data could not be generated because pseudo-first order did not give any measure of fit to the kinetic data.

(II) PSEUDO-SECOND ORDER MODEL

The pseudo-second order adsorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad [2]$$

Where

K_2 (g/mg/min) is the rate constant of pseudo-second order adsorption.

q_e and q_t (mg/g) respectively, are the sorption capacity at equilibrium and at time t .

For the boundary conditions $t=0$ to $t=t$ and $q_i=q_t$, the integrated form of the above equation becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad [3]$$

This is the integrated rate law for a pseudo-second order reaction. The rate equation can be rearranged to obtain;

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + t/q_e} \quad [4]$$

This has a linear form;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + 1/q_e t \quad [5]$$

Where h_o can be regarded as the initial rate as $(t/q_t) \rightarrow 0$ hence h_o (mg/g/min)

$$h_o = K_2 q_e^2 \quad [6]$$

The equation becomes

$$\frac{t}{q_t} = \frac{1}{h_o} + 1/q_e (t) \quad [7]$$

A plot of t/q_t versus t gives a linear relationship from which q_e and K_2 can be determined from the slope and intercept of the plot, respectively (C.Theivarasu *et.al.*, 2010).

The pseudo-second order rate equation was tested for the sorption of Pb²⁺ on CMSh 150µm and 250µm, respectively. Table 2, presents data for the pseudo-second order constants. The variation of t/q_t with time from the pseudo-order equation fits the adsorption of Pb²⁺ by the adsorbents is shown in figures 2 and 3.

TABLE 2: PSEUDO SECOND ORDER CONSTANTS FOR CMSh 150µm AND 250µm

CONSTANTS	LEAD (II) ION	
	CMSh 150µm	CMSh 250µm
R ²	0.9970	0.9970
K ₂ (gmg ⁻¹ min ⁻¹)	0.264	0.316
h _o (m ² g ⁻¹ min ⁻¹)	5.325	10.471
q _e (m ² g ⁻¹)	4.494	5.760

The results obtained show a highly significant linear relationship between the ions sorbed by the various adsorbents. The correlation coefficient (R²) values are high (0.9452 to 1.0000) showing that pseudo second order model gave the best fit and describes the adsorption of Lead (II) ion of all the adsorbents.

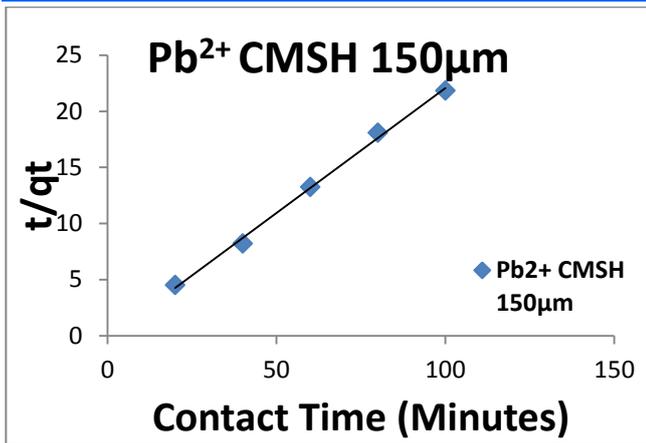


Fig 2: Pseudo Second Order Isotherm Model of Pb²⁺ CMSH 150µm

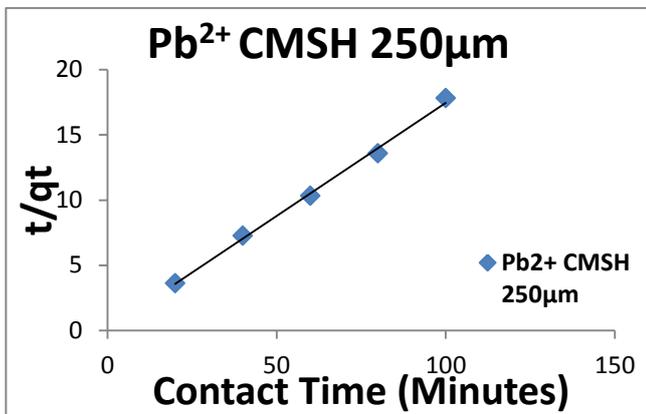


Fig 3: Pseudo Second Order Isotherm Model of Pb²⁺ CMSH 250µm

(III) ELOVICH ISOTHERM MODEL

Elovich model equation was also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation given below. The linear form of this equation is given by (S. M. Yakout and E. Elsherif, 2010):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad [8]$$

Where α is the initial adsorption rate (mg/g min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The Elovich coefficients could be computed from the plots q_t versus $\ln t$. The initial adsorption rate, α , and desorption constant, β , were calculated from the intercept and slope of the straight-line plots of q_t against $\ln t$.

Table 3 lists the kinetic constants obtained from the Elovich equation. It will be seen that applicability of the simple Elovich equation for the present kinetic data indicates that the Elovich equation was unable to describe properly the kinetics of the metal ion on the adsorbents of the two pore sizes. The value of α and

β varied as a function of the solution temperature. Also, the experimental data did not give a good correlation for these results.

TABLE 3: CALCULATED VALUES OF ELOVICH ISOTHERM MODEL CONSTANTS OF ADSORBENTS 150µm AND 250µm

CONSTANTS	Pb ²⁺ 150 µm	Pb ²⁺ 250 µm
R ²	0.0008	0.3113
B(gmg ⁻¹)	121.951	6.878
α (mgg ⁻¹ min ⁻¹)	1.023e+244	2.560 X1014

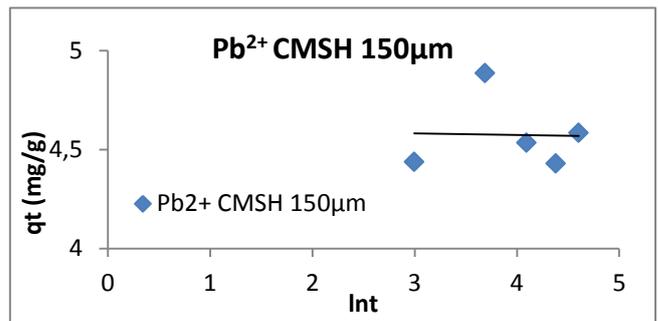


Fig 4: Elovich Model of Pb²⁺ CMSH 150µm

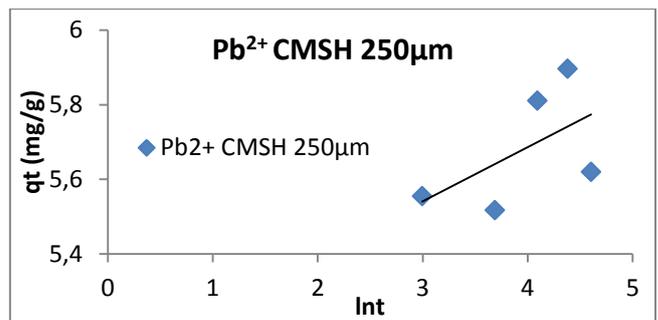


Fig 5: Elovich Model of Pb²⁺ CMSH 250µm

(c) ADSORPTION MECHANISMS

(1) LIQUID FILM DIFFUSIVITY MODEL

The kinetics of adsorption of metal ions on various adsorbents may be controlled by several independent processes such as bulk diffusion, external mass transfer, film diffusion, chemical reaction, and intra particle diffusion. Itodo et al., (2010) used the linear driving force concept and developed a simple relationship:

$$\ln(1 - \alpha_e) = -K_p t + D_F \quad [9]$$

Here $\alpha_e = q_t/q_e$ is the fractional attainment of equilibrium and K_p is the rate constant.

A plot of $\ln(1 - \alpha_e)$ versus time (t) yields the K_p the rate constant (min⁻¹) as the slope of the graph and a dimensionless constant D_F as intercept. If a plot of $\ln(1 - \alpha_e)$ against t is a straight line, then adsorption is controlled by particle diffusion and the diffusion of the metal ions to the adsorbent surface is independent of the initial concentration of the metal ions, if it is not a straight line, then it indicates that the sorption process is controlled by film- diffusion. The fractional attainment at equilibrium is the ratio of the amounts of

sorbate removed from solution after a certain time to that removed when sorption equilibrium is attained. It would definitely be expected that factors such as the number of reactive sites on the substrate and the bulkiness of the substrate would affect the rate of sorption. However, a great deal of information is gotten from the fractional attainment of equilibrium. The rate of attainment of equilibrium may be either film diffusion controlled or particle-diffusion controlled, even though this two different mechanism cannot be sharply demarcated (Itodo *et. al.*, 2010).

Table 4: LIQUID FILM DIFFUSIVITY CONSTANTS FOR CMSH 150µm AND 250µm

CONSTANTS	Pb ²⁺ 150 µm	Pb ²⁺ 250 µm
R ²	0.8144	0.6359
K _p (min ⁻¹)	20X10 ⁻⁵	50X10 ⁻⁵
D _F	-0.0193	-0.0512

The relative low R² values suggest that the diffusivity model does not entirely support the adsorption of Pb²⁺ using the various adsorbents and their two pore sizes. The diffusion rate constant K_p and the linear driving force D_F (diffusion parameter) obtained from the slope and intercepts of the plots are presented in table 4. A look at figures 6 and 7 shows that the plots are not very linear; suggesting that the sorption process is not particle diffusion controlled rather film diffusion controlled. The low R² also confirm this. Hence, the particle diffusivity model parameters were then used as film-diffusion controlled. The plots confirmed that the sorption rate of attainment of equilibrium is film-diffusion controlled. This implies that the time of uptake of metal ion on the surface of the adsorbent is dependent on the initial metal ion concentration of the adsorbate.

Consequently, in an adsorption process, the metal ions from the bulk solution should move through the thin liquid film surrounding the adsorbent. The thin film may produce a diffusion barrier for the metal ion to penetrate before they arrive at the binding sites on the adsorbent. This suggests that the metal ion must overcome this film barrier to be adsorbed at the sites on the adsorbent. This mechanism is consistent with the fact that the rate of diffusion of the metal ion also affects adsorption rate. This conclusion was also arrived at by Abia and Asuquo (2005) in their study on Pb²⁺, Ni²⁺, Cd²⁺ and Cr³⁺ with oil palm fibre; (Quadeer and Akhtar, 2005) in their study on Pb²⁺ sorption with activated carbon.

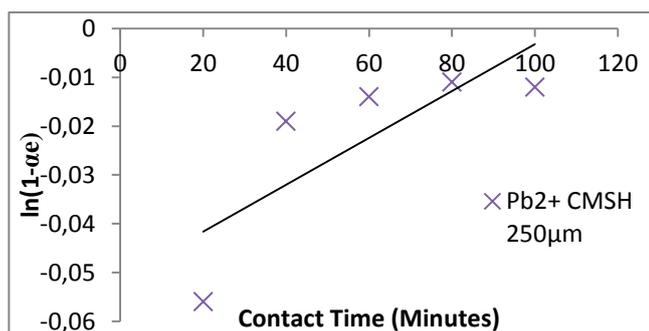


FIG 6 LIQUID FILM DIFFUSIVITY MODEL FOR CMSH 250µm

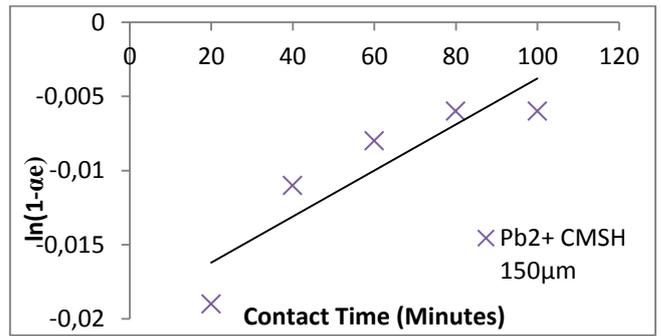


FIG 7 LIQUID FILM DIFFUSIVITY MODEL FOR CMSH 150µm

(2) MASS TRANSFER MODEL

The mass transfer kinetic model is generally expressed as (Abia *et al.*, 2006)

$$C_o - C_t = Dexp(K_o t) \quad [10]$$

Where,

C_o is the initial metal ion concentration (mg/l)

C_t is the metal ion concentration at time t in mg/l

T is the shaking time in minutes

D is the fitting diameter

K_o is a constant which is the mass transfer adsorption coefficient

A linearized form of the equation is written thus:

$$\ln(C_o - C_t) = \ln D + K_o t \quad [11]$$

If the sorption of the metal ion is depicted by the mass transfer model, then the plot of ln(C_o-C_t) versus time should give a linear relationship from where lnD and K_o can be determined from the intercept and slope of the plot, respectively.

Table 5: MASS TRANSFER CONSTANTS FOR CMSH 150µm AND 250µm

CONSTANTS	Pb ²⁺ 150 µm	Pb ²⁺ 250 µm
R ²	0.0214	0.2322
D	29.125	23.152
K _o	0.002	-0.0008

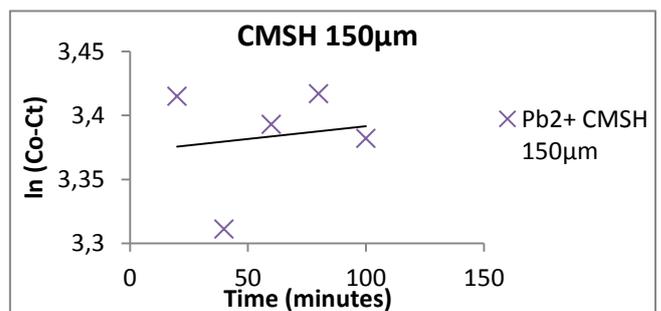


Fig 8: Mass Transfer Model of Metal Ions of Sample Pore Size CMSH 150µm

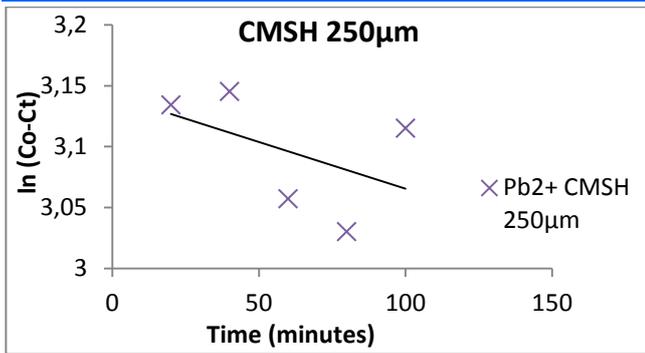


Fig 9: Mass Transfer Model of Metal Ions of Sample Pore Size CMSH 250µm

From the results, the relative low R^2 values suggest that the mass transfer diffusivity model does not support the adsorption of Pb^{2+} using the various adsorbents and their two pore sizes. Mass transfer is the movement of chemical species in a fluid mixture caused by some forms of driving force. There are two main mechanisms of mass transfer: diffusion and mass transport by convection (Aikpokpodion Paul E. *et al.*, 2013). The diffusion rate constant K_o and D (fitting parameter) obtained from the slope and intercepts of the plots are presented in table 5. A look at figures 8 and 9 shows that the plots are not very linear; suggesting that the sorption process is not diffusion and mass transport by convection controlled. The low R^2 values confirm this. Hence, diffusivity model parameters were then used as film-diffusion controlled. Aikpokpodion Paul E. *et al.*, 2013 stated that the rate of diffusion of ions between soil solution and soil surfaces is generally low due to molecular collisions that give rise to extremely strong hindrance to the movement of molecules.

(3) INTRA PARTICLE DIFFUSIVITY MODEL

Intra particle diffusivity equation for description of sorption kinetics was explored using the intra-particle diffusivity model given below (Hassan Zavvar *et al.*, 2012):

$$q_t = k_{id}t^{1/2} + C \quad [12]$$

Where,

k_{id} is the rate of sorption controlled by intra particle diffusivity ($mgg^{-1}min^{-1(1/2)}$)

C depicts the boundary layer thickness.

This model predicts that the plot of q_t versus $t^{1/2}$ should be linear with k_{id} and C as slope and intercept respectively if intra particle diffusivity is involved in the sorption process. Intra particle diffusivity is the rate controlling step if the line passes through the origin.

Table 6: INTRA PARTICLE FILM DIFFUSIVITY CONSTANTS FOR CMSH 150µm AND 250µm

CONSTANTS	Pb ²⁺ 150 µm	Pb ²⁺ 250 µm
R+	0.0084	0.2811
$K_{id}(mgg^{-1}min^{-1(1/2)})$	-5.22X10-2	2.69X10-1
C	30.892	35.846

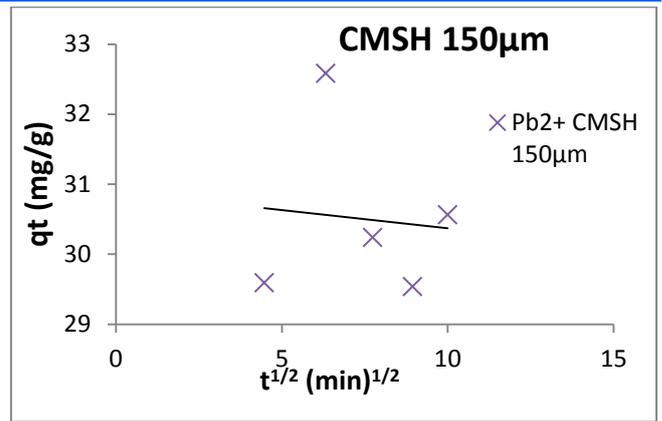


Fig 10: INTRA PARTICLE DIFFUSIVITY MODEL FOR CMSH 150µm

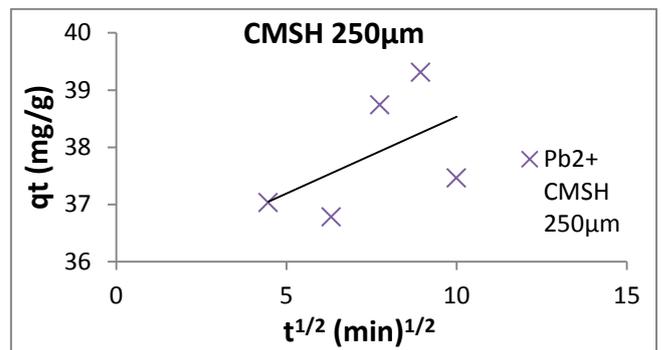


Fig 11: INTRAPARTICLE DIFFUSIVITY MODEL FOR CMSH 250µm

According to Itodo A.U *et al.*, 2010, of the intraparticle diffusivity plot, the sorption mechanism assumes intra particle diffusivity model if the following conditions are met:

1. High R^2 values to ascertain applicability
2. Straight line which passes through the origin for the plot area q_t versus $t^{1/2}$
3. Intercept $C < 0$.

A validity test which deviates from 2 and 3 above shows that the mode of transport is affected by more than one process (Hameed, 2009).The intercept C values are very high (well above zero values).

Higher values of k_{id} illustrate an enhancement rate of adsorption, whereas, larger k_{id} values illustrate better adsorption which is related to improved bonding between adsorbate and adsorbent particles (Itodo A.U *et al.*, 2010). From the assertion above, the values of k_{id} are relatively very low showing that there is no enhancement rate of adsorption which illustrates no adsorption and no better bonding between adsorbate and adsorbent particles.

From the results obtained in table 6, it shows that none of these conditions (1, 2 and 3) listed above were met suggesting that the intraparticle diffusivity model adsorption mechanism does not in any way favour the adsorption of Pb^{2+} of the same adsorbent of the two different pore sizes.

(4) INTRA PARTICLE DIFFUSION MODEL

The intraparticle diffusion model, according to (Akpokpodion Paul E. *et al.*, 2013) (A.A. Abia *et al.*, 2007) is expressed as:

$$R = K_{id}(t)a \quad [13]$$

Linearising the equation, becomes

$$\log R = \log K_{id} + a \log t \quad [14]$$

Where,

R is the percent of metal ion adsorbed

t is the contact time in minutes

a is the slope on a logarithmic plot which depicts the adsorption mechanism

K_{id} is the intra particle diffusion rate constant which is taken as a rate factor, that is, percent of the sorbate adsorbed per unit time ($\text{mgg}^{-1}\text{min}^{-1(1/2)}$)

If the sorption can be represented by the model, a plot of $\log R$ versus $\log t$ should yield a linear relationship with a slope **a** and an intercept **$\log K_{id}$** .

According to (Akpokpodion Paul E. *et al.*, 2013), this model is based on the assumption that, diffusion into the interior pores of the soil particles from the soil solution controls the adsorption of Mg^{2+} onto the studied soils.

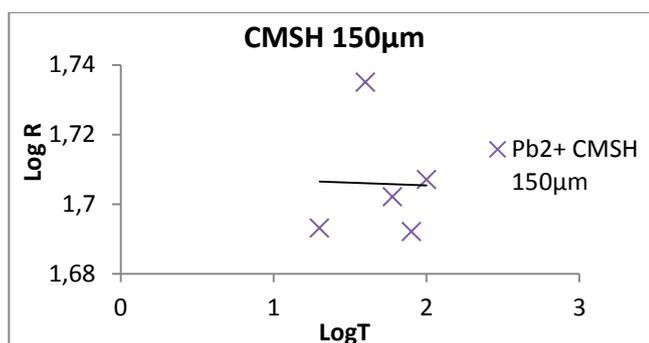


Fig 13: INTRA PARTICLE DIFFUSION MODEL FOR CMSH 150µm

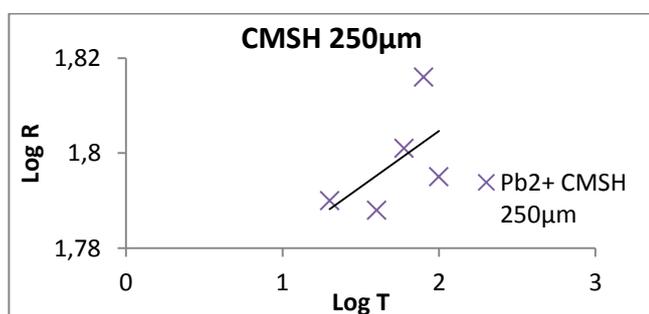


Fig 14: INTRA PARTICLE DIFFUSION MODEL FOR CMSH 250µm

From the results obtained in table 7, it follows that R^2 , K_{id} and a values are low suggesting that the intraparticle diffusion model adsorption mechanism does not in favour the adsorption of the metal ion of the adsorbent of the pore size except 250µm whose R^2 value was 0.8420. This means that the values of K_{id}

being relatively very low shows that there is no enhancement rate of adsorption which illustrates no adsorption and no better bonding between sorbate and sorbent particles. Higher values of K_{id} illustrate an enhancement rate of adsorption, whereas, larger K_{id} values illustrate better adsorption which is related to improved bonding between sorbate and sorbent particles (Itodo A.U *et al.*, 2010).

Table 7: INTRA PARTICLE FILM DIFFUSION CONSTANTS FOR CMSH 150µm AND 250µm

CONSTANTS	Pb ²⁺ 150 µm	Pb ²⁺ 250 µm
R^2	0.0007	0.8420
a	1.6X10-3	1.11X10-2
$K_{id}(\text{mgg}^{-1}\text{min}^{-1(1/2)})$	0.2326	0.2507

(c) PORE SIZE ANALYSIS

One of the most important adsorbent parameters is the pore size and pore size distribution. Adsorbent surface area is the factor directly affecting the analyte retention. Pore size is defined as the ability of the analyte molecules to penetrate inside the particle and interact with its inner surface. This is especially important because the ratio of the outer particle surface to its inner one is about 1:1000. The surface molecular interaction mainly occurs on the inner particle surface. Micro-pores are easily accessible to the analytes since there is little or no steric hindrance effect. Meso-pores are partially accessible but molecular diffusion into the pore spaces are restricted by steric hindrance effect which significantly slows mass transfer and decreases the adsorption efficiency.

From the results in the table above, the two pore sizes can be used to adsorb the metal ions efficiently. Although, 150µm had faster rate of adsorption than 250µm, the values obtained from 250µm, still indicate that the pore size is effective to use and can equally serve as a good low cost adsorbent for the sorption of Pb^{2+} from aqueous solution.

CONCLUSION:

The conclusions based on experimental study were:

- (i) Adsorbent preparation by carbonization and chemical modification of biosorbent using Mercapto acetic acid showed good affinity for the metal ion (Pb^{2+}).
- (ii) The result obtained can be used for design purposes.
- (iii) These results can be used as a basis for the study of desorption and recovery of Lead from solution.
- (iv) Pore size analysis showed that 150µm mesh had faster adsorption rate than 250µm mesh, although both recorded high adsorption values.

REFERENCE

1. Abia .A.A. and Igwe, J.C. (2005). *Sorption kinetics and intra particulate diffusivities of Cd,*

- Pb and Zn ions on maize cob*. African Journal of Biotechnology 4(6):509-512
2. Abia, A.A, Asuquo, E.D (2007) "Kinetics of cd^{2+} and cr^{3+} sorption from aqueous solutions using Mercaptoacetic acid modified and unmodified oil palm fruit fibre (*Elaeis guineensis*) Adsorbents" *Tsinghua Science and technology* 12 (4) pp485-492
 3. Aikpokpodion Paul E, Osobamiro T, Atewolara-Odudu O. C, Oduwole O. O. and Ademola S. M (2013) "Studies on adsorption mechanism and kinetics of magnesium in selected cocoa growing soils in Nigeria". *Journal of Chemical and Pharmaceutical Research*, 2013, 5(6):128-139
 4. B.H Hameed, D.K Mahmoud, A.L Ahmad (2008) "Equilibrium Modeling And Kinetic Studies On The Adsorption Of Basic Dye By A Low-Cost Adsorbent:Coconut(*Cocos nucifera*) Bunch Waste". *Journal of Hazardous Materials* 158(2008)65-72
 5. Babarinde N.A.A;Babalola J.O;Adebisi, O.B (2008) "Kinetic, Isotherm and Thermodynamic Studies of the Biosorption of Zinc(II) from Solution by Maize Wrapper". *International Journal of Physical Sciences* Vol3(2) Pp 050-055.
 6. Demirbas Ozkan, Alkan Mahir (2011) "Thermodynamics, Kinetics and Adsorption properties of some Biomolecules onto mineral surfaces" In Tech ISBN 978-953-307-627-0 . DOI: 10.5772/22833
 7. Hassan Zavvar Mousavi, A bdorrahman Hosseinifar and Vahdat Jahed (2012) "Studies of the adsorption thermodynamics and kinetics of Cr(III) and Ni(II) removal by polyacrylamide". *J. Serb. Chem. Soc.* 77 (3) 393–405 (2012) 393-405
 8. Horsfall, M. Jnr. Abia, A.A. and Spiff, A.I. (2004). *Studies on the Influence of Mercaptoacetic Acid (MAA) modification of Cassava (Manihot esculenta Cranz) Waste biomass on the Adsorption of Cu^{2+} and Cd^{2+} from Aqueous Solution*. Bull Korean chem. Soc. 25(7): 969-976.
 9. Imaga, C, Abia, A.A, Igwe, J.C. (2014) "Removal of Ni (II), Cu (II), and Zn (II) ions from synthetic waste water using sorghum hull as adsorbents." *Pelagia research library. Der Chemica Sinica*
 10. Imaga, C.C., Abia, A.A (2014) "Assessment of Chemical Modification, ph and pore size of Sorghum (*Sorghum bicolor*) in sorption of Ni^{2+} and Cu^{2+} Science Journal of Pure and Applied Chemistry. Vol.2014(2014)
 11. Itodo A.U., Abdulrahman F.W, Hassan L.G, Maigandi S.A., Itodo H.U (2010) "Intraparticle Diffusion and Intraparticulate Diffusivities of Herbicide on Derived Activated Carbon". <http://www.sciencepub.net/researcher>. (2010) 74 - 86
 12. M.Urik; P. Littera; J.Sevc; M.Kolencik; S.Cernansky (2009) "Removal of Arsenic (V) from Aqueous Solutions Using Chemically Modified Sawdust of Spruce(*Picea abies*): Kinetics and Isotherm Studies". *Int.J. Environ. Sci. Tech.*, 6(3), 451-456
 13. Opeolu, B.O; Bamgbose, O; Arowolo, T.A; Adetunji, M.T.; (2009) "Utilization of Maize (*Zea mays*) Cob as an adsorbent for lead(II) removal from aqueous solutions and industrial effluents". *African Journal of Biotechnology*. Vol 8 (8) pp1567-1573.
 14. Qadeer, R and Akhtar, S. (2005) "Kinetic Study Of Lead Ion Adsorption On Activated Carbon. *Turk. J. Chem.* 29:95-99
 15. S. M. Yakout and E. Elsherif (2010) "Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons". *Applied Science Innovations Pvt. Ltd., India Carbon – Sci. Tech.* 1 (2010) 148 – 149
 16. Suleman Qaiser, Anwar R. Saleemi, Muhammad Umar (2009) "Biosorption Of Lead (II) And Chromium (VI) On Groundnut Hull: Equilibrium, Kinetics And Thermodynamic Study." *Electronic Journal Of Biotechnology* Vol.12 No4
 17. Theivarasu C., Mysamy S. (2010) "Equilibrium and Kinetic Adsorption studies of Rhodamine – B from aqueous solutions using cocoa (*Theobroma cacao*) shell as a new adsorbent". *International journal of engineering science and Technology* vol. 2 (II), 2010, 6284-6292
 18. Zolgharnein, J.; Asanjarani, N. and Shariatmanesh, T. (2011) "Removal of Thallium (I) from Aqueous Solution using Modified Sugar beet Pulp". *Toxicological and Environmental Chemistry*, 93:2,207-214.