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# A Comparative Study of Adsorption Kinetics and Mechanisms of Zinc (II) Ion Sorption using Carbonized and modified Sorghum (*Sorghum Bicolor*) Hull of two Pore Sizes (150μm and 250μm)

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Imaga C. C. [α] & Abia A. A [σ]

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## I. Introduction

Adsorption, an established industrial separation technique used in bulk separation technique uses both bulk/batch separation and purification suited for the solution of such problems. 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 (Imaga C.C and Abia A.A, 2015). 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.

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(Imaga C.C and Abia A.A, 2015).

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.

### *a) ZINC*

Zinc is one of the commonest elements in the earth's crust. It's found in air, soil, and water, and is present in all foods. Pure Zinc is a bluish-white shiny metal. Zinc has many commercial uses as coating to prevent rust, in dry cell batteries, and mixed with other metals to make alloys like brass and bronze. Zinc is released into the environment by natural processes, but most comes from activities of people like mining, steel production, coal burning, and burning of waste. It attaches to soil, sediments, and dust particles in the air. Harmful health effects generally begin at levels from 10-15 times the RDA (in the 100 to 250 mg/day range). Eating large amounts of Zinc, even for a short time, can cause stomach cramps, nausea, and vomiting. Taken

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longer, it can cause anemia, pancreas damage, and lower levels of high-density lipoprotein cholesterol (HDL - the good form of cholesterol). Environmental toxicity of Zinc in water is dependent upon the concentration of other minerals and the pH of the solution, which affect the ligands that associate with Zinc (Heijerick *et al*., 2002a; Paquin *et al*., 2002; Santore 2002). Zinc is often present in soils and grasses as a result of atmospheric deposition. Soil pH limits the mobilization of Zinc in soil. Thus, Zinc from tire debris will be less available and become immobile with soil interactions (Smolders and Degryse 2002). Zinc tends to sorb more readily at a high pH (pH >7) than at a low pH (EPA 1979d). Zinc is capable of forming complexes with a variety of organic and inorganic groups (ligands).

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 Zinc (II) ion from aqueous solution in a batch sorption system. The effects of contact time,mechanisms and sorption kinetics of the carbonised and Mercapto-acetic acid modification and Particle size were investigated.

## II. 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.

### a) *Methods*

#### i. *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 (Imaga C.C and Abia A.A, 2015).

#### ii. *Activation of Sorghum Hulls*

The screened fine Sorghum Hulls powder was further soaked in excess of 3.0M $HNO_3$ 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 $HNO_3$ 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 (Imaga C.C and Abia A. A, 2015).

#### iii. *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 according to (Imaga C.C and Abia A.A, 2015).

#### iv. *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 ($HSCH_2COOH$) 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.(Imaga C.C and Abia A.A, 2015)

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 CMSH 150*μ*m and 250*μ*mwere stored in air tight plastic containers and labelledrespectively. (Imaga C.C and Abia A.A, 2015)

#### v. *Preparation of Adsorbate Solutions for Sorption Studies*

A stock solution of 1000ppm of the metal Zinc was prepared from Zinc Chloride ($ZnCl_2$); assay 98% (Halewood Chemicals Limited). Thereafter, serial dilution was carried out on the stock solution to obtain working solution of 60 ppm of the Zinc (II) ion. The concentration of the standard was confirmed using an Atomic Adsorption Spectrophotometer .The pH of the solution was kept at 7.0.

#### vi. *Sorption Studies at Different Contact Time*

Kinetics of sorption studies were carried out according to the method described by Imaga C.*etal*., 2014. Kinetics of sorption for $Zn^{2+}$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).30cm$^3$ of standard solution of the metal, initial concentration of 60mg/l was transferred into various 250cm$^3$ 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 and100 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 20cm$^3$ 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).

## III. 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 $Zn^{2+}$ adsorbed by the adsorbents CMSH 150µm and 250µm 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 figure1.

*Table 1 :* Effect Of Contact Time On Amount Of Zinc (II) Ion Adsorbed For CMSH 150*µm* And 250*µm*

| Contact Time(Mins) | Amount Of Metal Ion Concentration Adsorbed | |
|---|---|---|
| | $Zn^{2+}$ 150*µm* | $Zn^{2+}$ 250*µm* |
| 20 | 55.045 | 55.115 |
| 40 | 55.152 | 55.059 |
| 60 | 55.117 | 55.196 |
| 80 | 54.993 | 55.072 |
| 100 | 55.017 | 55.158 |

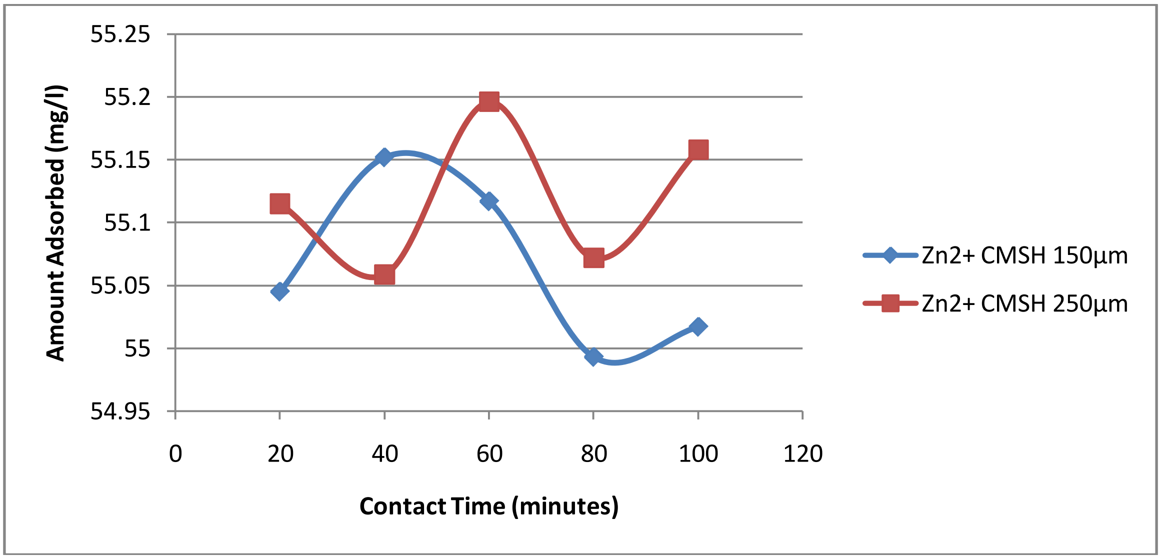

*Figure 1 :* Graph of Amount Adsorbed versus Contact Time for $Zn^{2+}$ (CMSH 150*µm* and 250*µm*)

The maximum sorption time for 150*µm* and 250*µm* were at 40th and 60th minutes (55.152mg/l and 55.196mg/l), respectively. The $Zn^{2+}$sorption is higher in 250*µm* than in 150*µm* except in the 40th minute. The rate of sorption in 150*µm* occurred faster (20th, 60th, 80th and 100th minutes) [55.045, 55.117, 54.993, 55.017]mg/l than in 250*µm*(20th, 60th, 80thand 100thminutes) [55.115, 55.196, 55.072, 55.158] mg/l, respectively except in the 40th minute where the adsorption of $Zn^{2+}$ was higher in 150*µm* than in 250*µm*.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. This also could be largely due to their variations in surface areas. However, the sorption of $Zn^{2+}$ by both 150*µm* and 250*µm* were very high.

### *b) Kinetic Modeling*

Quantification of the changes in sorption of metals with time requires the use of appropriate kinetic model. The kinetic models-Elovich model, Pseudo first and Second order models were employed to investigate the kinetics of sorption of the divalent $Zn^{2+}$ by the adsorbents.

i. *Pseudo-First Order Model*

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

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (1)$$

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 $gmg^{-1}.min^{-1}$

The plot of the pseudo- first order of $Zn^{2+}$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:

$$\frac{dqt}{dt} = K_2(q_e - q_t)^2 \qquad (2)$$

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 $q_t=q_t$, the integrated form of the above equation becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \qquad (3)$$

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

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + t/q_e} \qquad (4)$$

This has a linear form;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + 1/q_e\, t \qquad (5)$$

Where $h_o$can be regarded as the initial rate as (t/qt)→ $0$ hence $h_o$(mg/g/min)

$$h_o = K_2 q_e^2$$

The equation becomes

$$\frac{t}{q_t} = \frac{1}{h_o} + 1/q_e(t)$$

A plot of t/qt 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 $Zn^{2+}$on CMSH 150µm and 250µm, respectively. Table 2, presents data for the pseudo-second order constants. The variation oft/qt with time from the pseudo- second order equation fits the adsorption of the $Zn^{2+}$by the adsorbents are shown in figures 2 and 3.

*Table 2 :* Pseudo Second Order Constants For CMSH 150*µ*m And 250*µ*m

| Constants | Zinc (Ii) Ion | |
|---|---|---|
| | CMSH 150*µm* | CMSH 250*µm* |
| $R^2$ | 1.0000 | 1.0000 |
| $K_2(gmg^{-1}min^{-1})$ | 1.457 | 4.430 |
| $h_o(mgg^{-1}min^{-1})$ | 99.010 | 303.030 |
| $q_e(mgg^{-1})$ | 8.244 | 8.271 |

The results obtained show a very highly significant linear relationship of the sorbed Zinc (II) ion by the various adsorbents CMSH 150*µ*m and CMSH 250*µ*m, respectively. The correlation coefficient ($R^2$) values are high (1.0000 each) showing that pseudo second order model gave the best fit and a good description of the sorption of Zinc (II) ionby the two adsorbents.

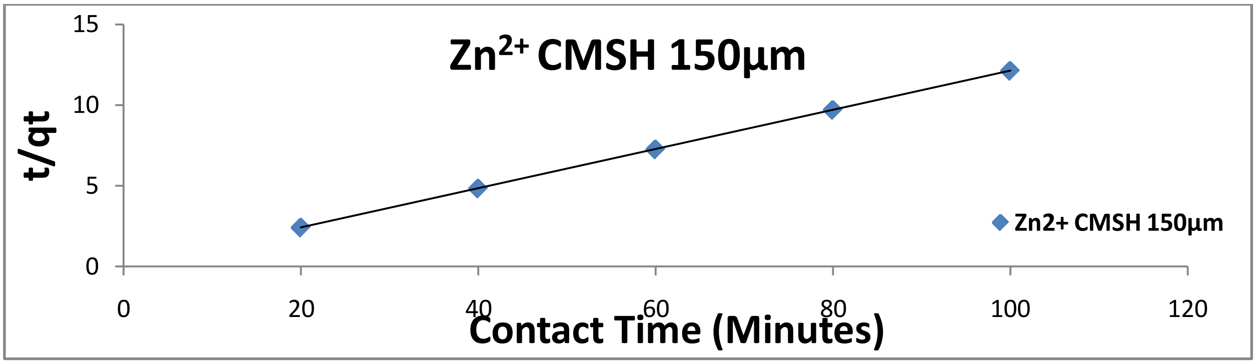

*Figure 2 :* Pseudo Second Order Isotherm Model of Zn$^{2+}$ CMSH 150µm

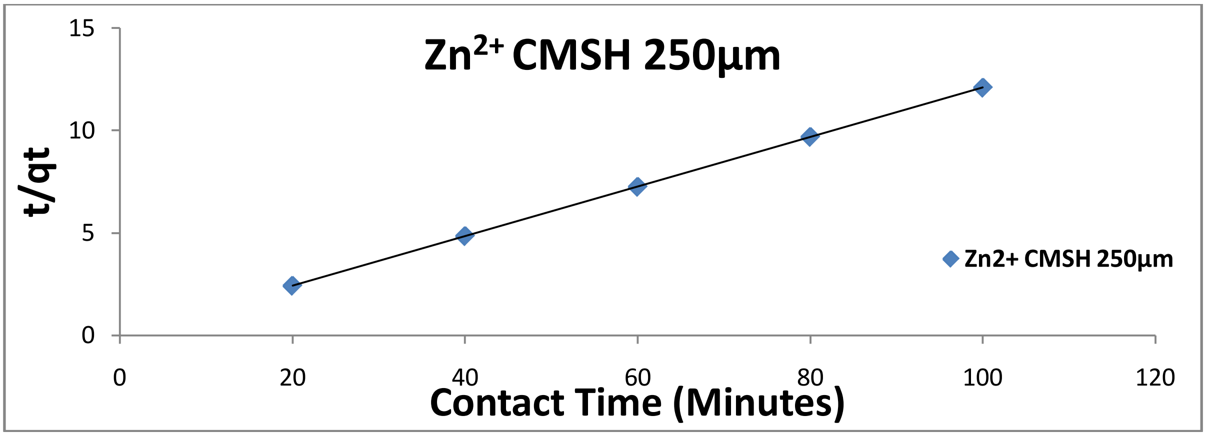

*Figure 3 :* Pseudo Second Order Isotherm Model of Zn$^{2+}$ CMSH 250µm

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):

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} lnt \qquad (8)$$

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 qt 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 qt against lnt. 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 αand 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 | Zn$^{2+}$ 150 µm | Zn$^{2+}$ 250 µm |
|---|---|---|
| $R^2$ | 0.1142 | 0.0722 |
| B(gmg$^{-1}$) | 185.185 | 277.778 |
| α(mgg$^{-1}$min$^{-1}$) | 5.691e+663 | 1.875e+993 |

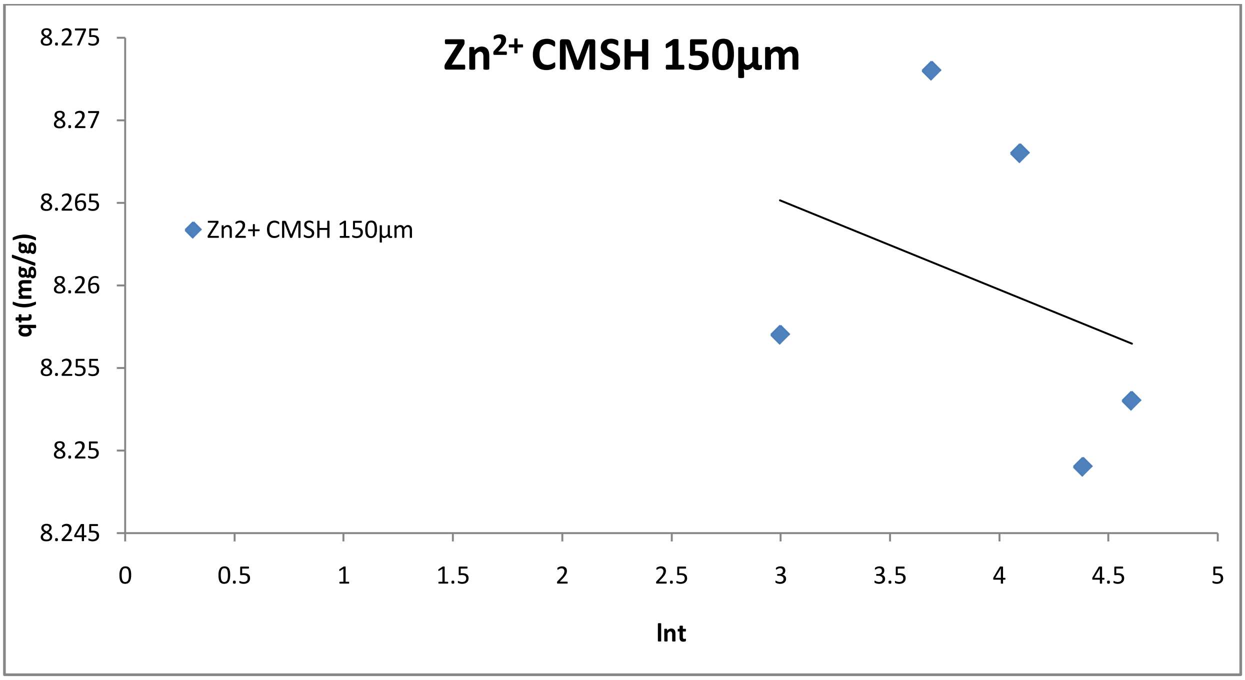

*Figure 4 :* Elovich Isotherm Model of $Zn^{2+}$ CMSH 150*µ*m

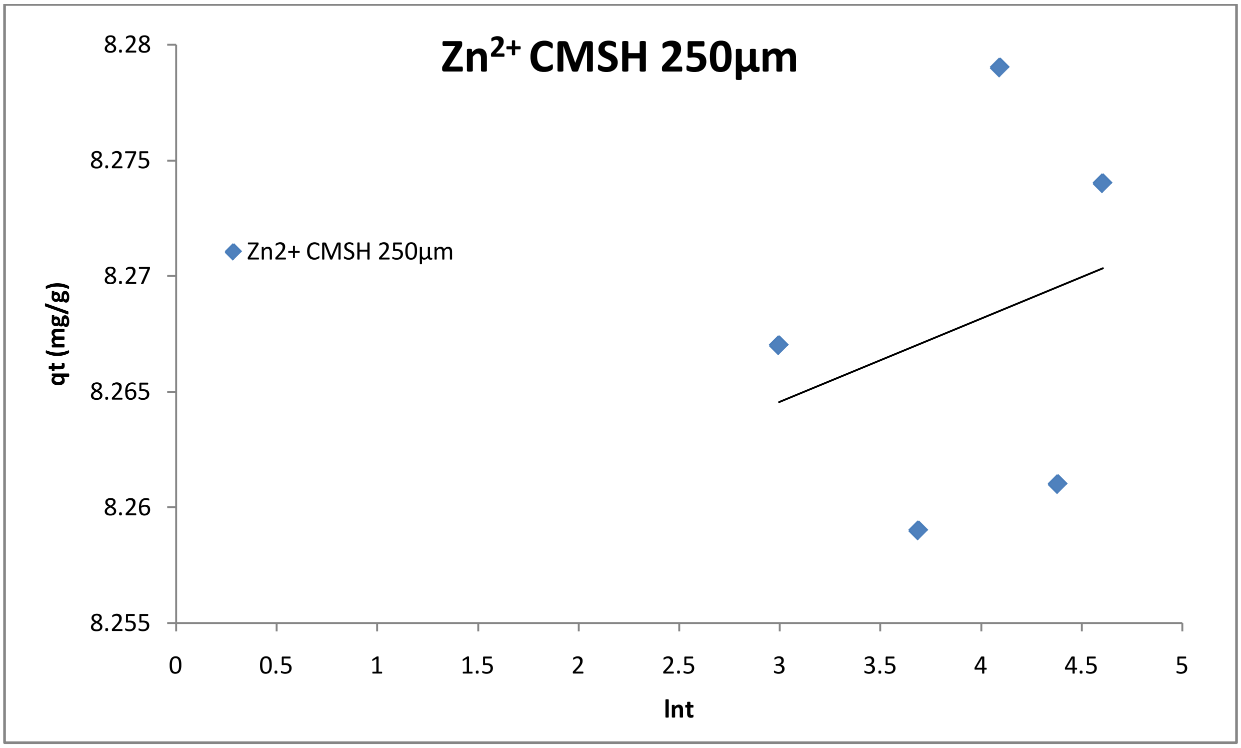

*Figure 5 :* Elovich Isotherm Model of $Zn^{2+}$ CMSH 250*µ*m

### c) *Adsorption Mechanisms*

#### i. *Liquid Film Diffusivity Model*

The kinetics of sorption of Zinc (II) ion onto two different adsorbents of different pore sizes may be controlled by several independent processes such as bulk diffusion, external mass transfer, film diffusion, chemical reaction, and intra particle diffusion.Imaga C.C and Abia A.A, 2015; Itodo *et al.*, (2010) used the linear driving force concept and developed a simple relationship:

$$\ln (1-\alpha_e) = -K_p t + D_F \qquad (9)$$

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. The diffusion of Zinc (II) ions to the adsorbent surface is independent of the initial concentration of the Zinc (II) ions.If it is not a straight line, then it indicates that the sorption process is film- diffusion controlled. 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 thesubstrate 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 these two different mechanisms cannot be sharply demarcated (Itodo *et. al.*, 2010).

*Table 4 :* Liquid Film Diffusivity Constants For CMSH 150*µ*m And 250*µ*m

| Constants | $Zn^{2+}$ 150 *µ*m | $Zn^{2+}$ 250 *µ*m |
|---|---|---|
| $R^2$ | 0.9098 | 0.9616 |
| Kp($min^{-1}$) | $40x10^{-5}$ | $50x10^{-5}$ |
| $D_F$ | -0.1107 | -0.1167 |

The $R^2$ values of $Zn^{2+}$150*µ*mand $Zn^{2+}$ 250*µ*msuggests that the diffusivity model does entirely support the sorption of $Zn^{2+}$using the two adsorbents and its 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 $Zn^{2+}$150*µ*m and $Zn^{2+}$250*µ*m areparticle diffusion controlled since the plotted graphsare linear. Since sorption of $Zn^{2+}$ 150*µ*m and $Zn^{2+}$ 250*µ*mare particle diffusion controlled (plot is linear), it could be affected by the following processes: (1) diffusion from the surface to the internal sites (surface diffusion or pore diffusion); (2) uptake which can involve several mechanisms: physicochemical sorption, ion exchange, precipitation or complexation (Igwe *et al.*, 2005); (3) diffusion of the solute from the solution to the film surrounding the particle;(4) diffusion from the film to the particle surface (external diffusion); The mechanism of sorption depicted to be particle diffusion controlled means that intraparticle mass transfer resistance is rate limiting(Igwe *et al.*, 2006). This means that in the presence of a mixture of the metal ions, the metal ions compete for the adsorption sites on the adsorbent.This competition affects the diffusion properties of the metal ions, hence decreases the adsorption capacity of the metal ions. The $R^2$values confirm this. Thus, the metal ion that successfully reaches the adsorption site faster depends on the above factors and also on the ionic radii of the metal ions. Competition among the metalions for adsorption sites clearly affected the adsorption capacity (Igwe *et al.*, 2005; Imaga C.C and Abia A.A, 2015).

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$Pb^{2+}$, $Ni^{2+}$, $Cd^{2+}$ and $Cr^{3+}$with oil palm fibre.

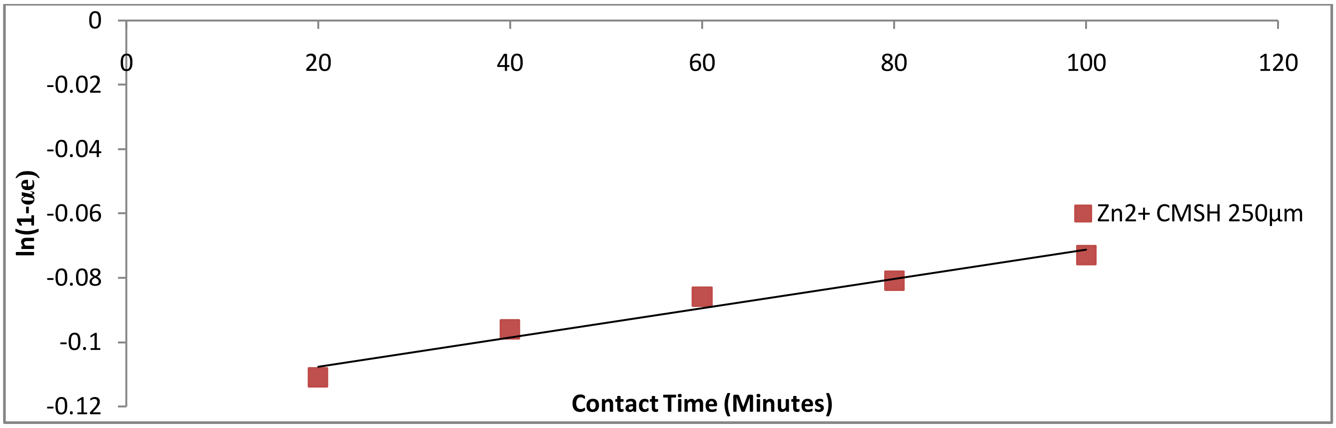

*Figure 6 :* Liquid Film Diffusivity Model For CMSH 250*µ*m

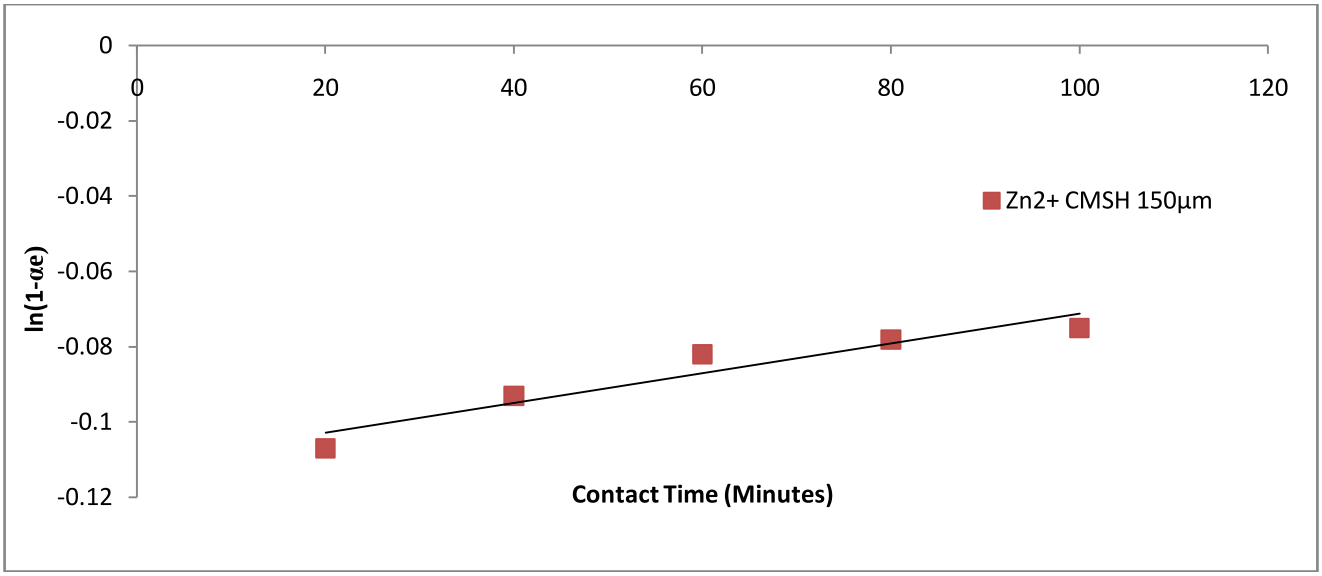

*Figure 7 :* Liquid Film Diffusivity Model For CMSH 150µm

ii. *Mass Transfer Model*

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

$$C_o - C_t = Dexp(K_o t) \qquad (10)$$

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:

$$\ln(C_o - C_t) = \ln D + K_o t \qquad (11)$$

If the sorption of the metal ion is depicted by the mass transfer model, then the plot of In ($C_o$-$C_t$) versus time should give a linear relationship from where InD 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 | $Zn^{2+}$ 150 µm | $Zn^{2+}$ 250 µm |
|---|---|---|
| $R^2$ | 0.2655 | 0.0789 |
| D | 4.871 | 4.911 |
| $K_O$ | 0.0002 | -0.0001 |

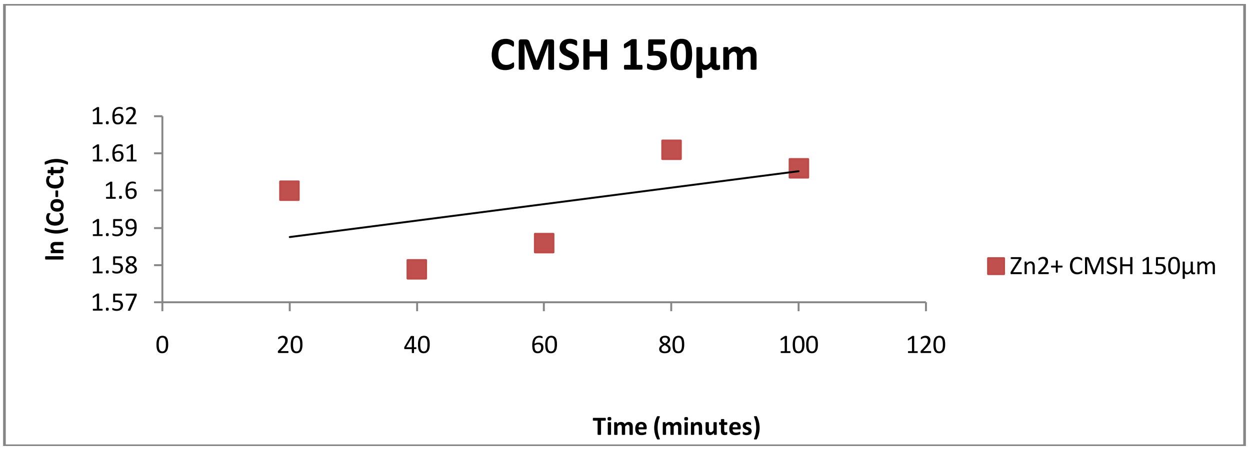

*Figure 8 :* Mass Transfer Model of Metal Ions of Sample Pore Size CMSH 150µm

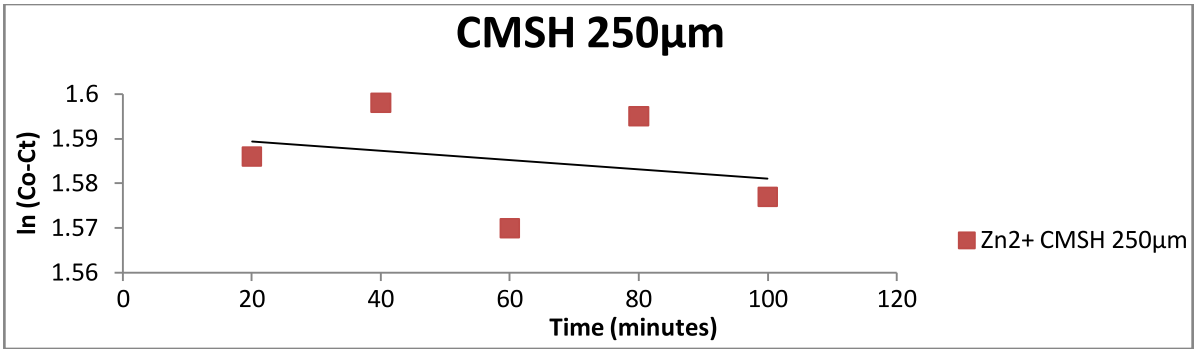

*Figure 9 :* Mass Transfer Model of Metal Ions of Sample Pore Size CMSH 250$\mu$m

From the results, the low $R^2$ values suggest that the mass transfer diffusivity model does not support the adsorption of the metal ions 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; Imaga C.C and Abia A. A, 2015). These mechanisms (diffusion and mass transport by convection) were not supported suggesting that mass transfer model does not favour the sorption of $Zn^{2+}$. 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 non- linear suggesting that the sorption process is not diffusion and mass transport by convection controlled. The confirmation is shown on their low $R^2$ values. Imaga C.C and Abia A.A, 2015stated 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.

iii. *Intra Particle Diffusivity Model*

Intra particle diffusivity equation for description of sorption kinetics was explored using the intra-particle diffusivity model given below (Imaga C.C and Abia A.A, 2015):

$$q_t = k_{id} t^{1/2} + C \qquad (12)$$

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 150$\mu$m And 250$\mu$m

| Constants | $Zn^{2+}$ 150 $\mu$m | $Zn^{2+}$ 250 $\mu$m |
|---|---|---|
| $R^2$ | 0.1858 | 0.0685 |
| $K_{id}(mgg^{-1}min^{-1(1/2)})$ | $-1.33 \times 10^{-2}$ | $6.9 \times 10^{-3}$ |
| C | 55.165 | 55.068 |

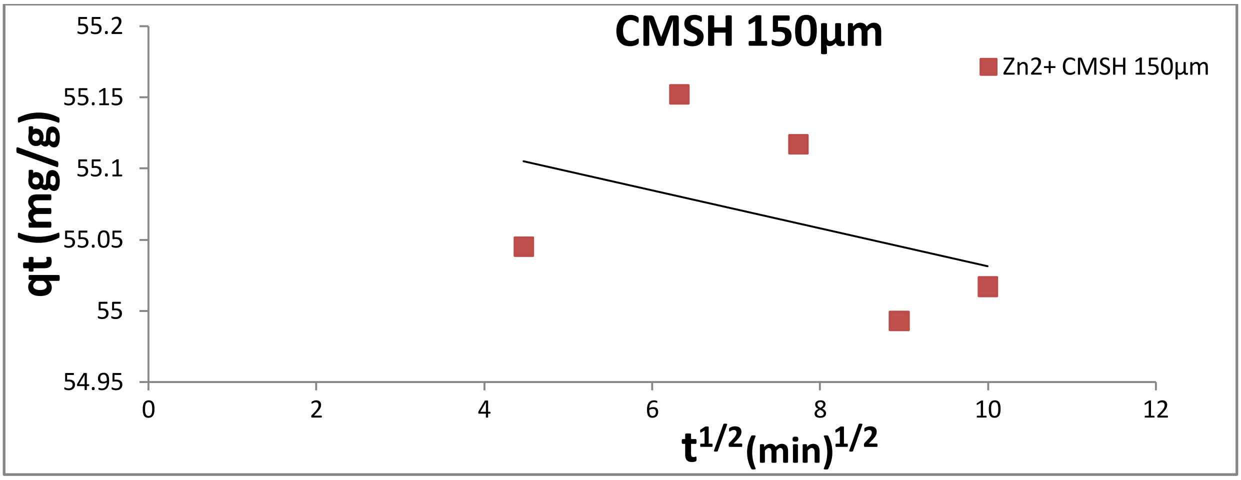

*Figure 10 :* Intra Particle Diffusivity Model For CMSH 150$\mu$m

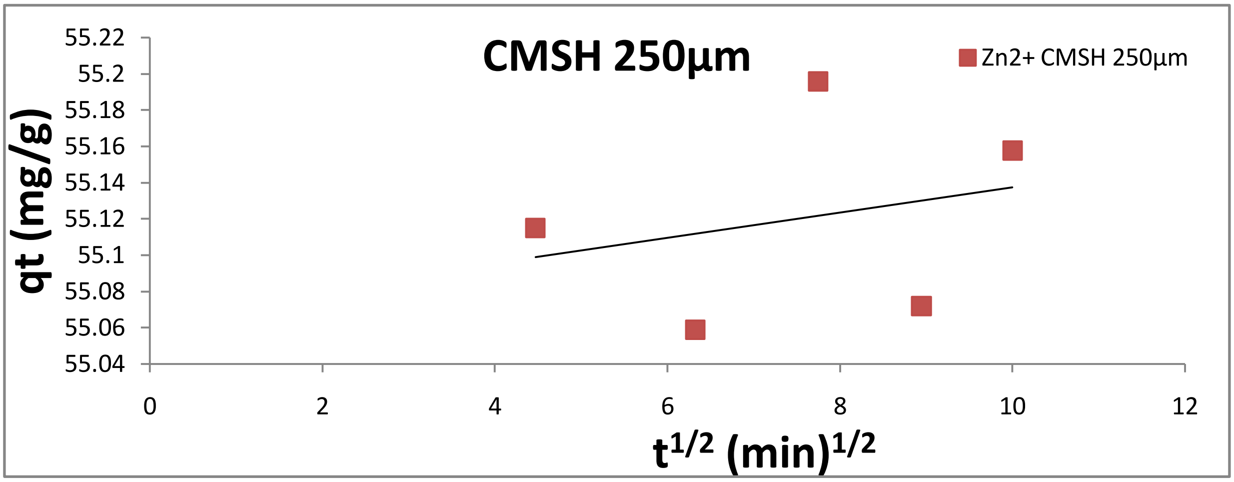

*Figure 11 :* Intraparticle Diffusivity Model For CMSH 250µm

According to (Itodo A.U *et al*., 2010; Imaga C.C and Abia A.A, 2015), 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; Imaga C.C and Abia A.A, 2015).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 $Zn^{2+}$with the adsorbent of the two different pore sizes.

### iv. *Intra Particle Diffusion Model*

The intraparticle diffusion model, according to (Imaga C.C and Abia A.A, 2015; Akpokpodion Paul E. *et al., 2013*; A.A. Abia *et al.,* 2007)is expressed as:

$$R = K_{id}(t)a \tag{13}$$

Linearising the equation, becomes

$$\log R = \log K_{id} + a \log t \tag{14}$$

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 ($mgg^{-1}min^{-1(1/2)}$)

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.

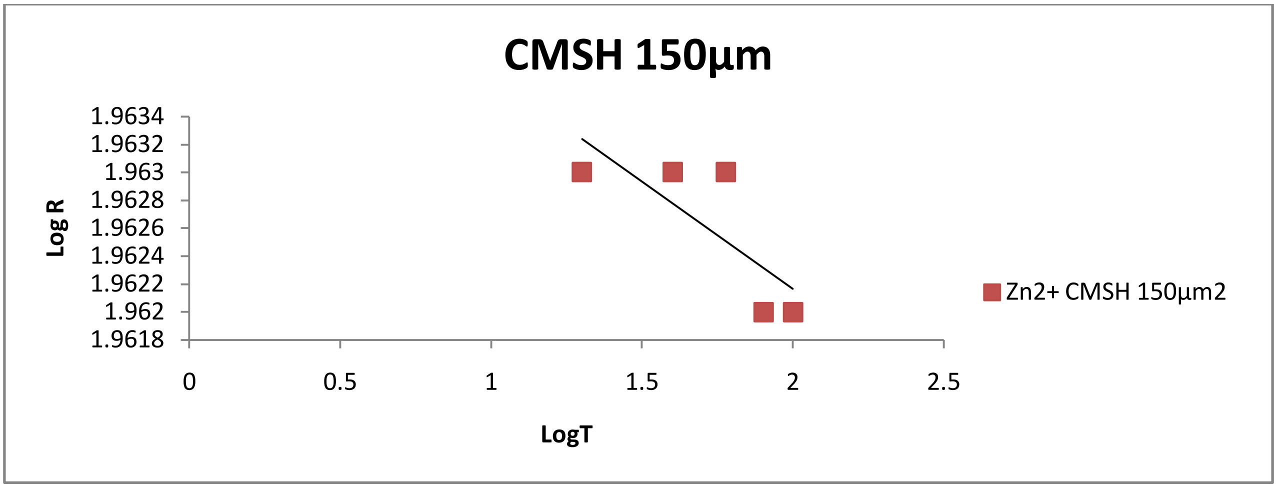

*Figure 13 :* Intra Particle Diffusion Model For CMSH 150*µ*m

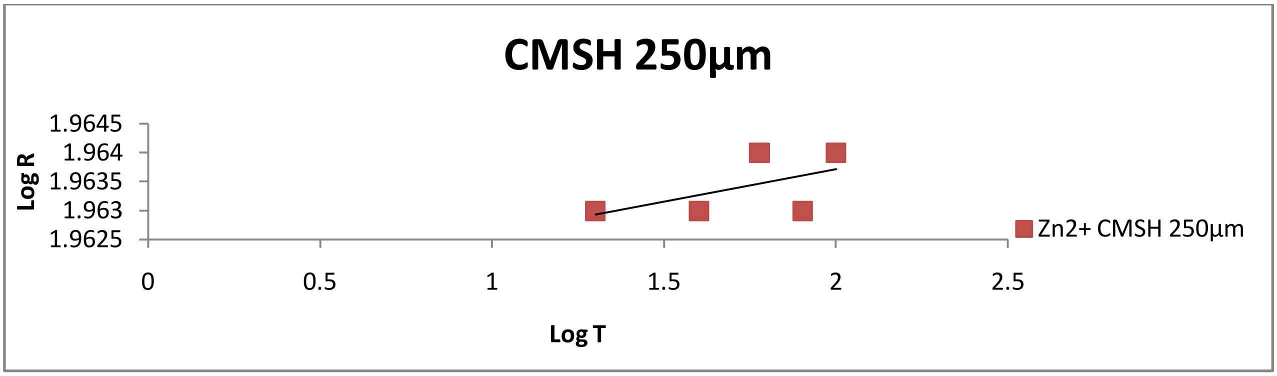

*Figure 14 :* Intra Particle Diffusion Model For CMSH 250*µ*m

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 any way favour the adsorption of $Zn^{2+}$with the adsorbent of the two pore sizes. This means that the values of $k_{id}$ being relatively very low shows that there is no enhancement rate of adsorption illustrating no sorption 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 (Imaga C.C and Abia A.A, 2015; Itodo A.U *et al.*, 2010).

*Table 7 :* Intra Particle Film Diffussion Constants For CMSH 150*µ*m And 250*µ*m

| Constants | $Zn^{2+}$ 150 *µ*m | $Zn^{2+}$ 250 *µ*m |
|---|---|---|
| $R^2$ | 0.6026 | 0.0632 |
| A | $-1.5 \times 10^{-3}$ | $-1.24 \times 10^{-2}$ |
| $K_{id}(Mgg^{-1}min^{-1(1/2)})$ | 0.2934 | 0.2986 |

## IV. 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 littleor 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 (Imaga C.C and Abia A.A).

From the results, the two pore sizes are effective to use and can equally serve as a good low cost adsorbent for the sorption of $Zn^{2+}$ from aqueous solution.

## V. 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 $Zn^{2+}$.
- (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 $Zn^{2+}$from solution.
- (iv) Pore size analysis showed that 150*μm* mesh had faster adsorption rate than 250*μm* mesh, although both recorded high adsorption values.
- (v) For liquid film diffusivity model, $Zn^{2+}$ 150*μm*and$Zn^{2+}$250*μm* favoured particle diffusion controlled adsorption.
- (vi) Mass transfer, Intra particle diffusivity, Intra particle diffusion and Elovich models did not favour the sorption of $Zn^{2+}$ using the adsorbent of the two different pore sizes.

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