



## KINETICS AND MECHANISMS OF CADMIUM (II) ION SORPTION USING CARBONIZED AND MODIFIED SORGHUM (*SORGHUM BICOLOR*) HULL OF TWO PORE SIZES (CMSH 150 $\mu$ m AND 250 $\mu$ m)

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### ABSTRACT

*Aim of this study was to investigate the use of modified and carbonized Sorghum Hull of two different pore sizes (150 $\mu$ m and 250 $\mu$ m) in the removal of Cadmium (II) ion from aqueous solution. The effect of contact time (20, 40, 60, 80 and 100) minutes were investigated, reported and analysed accordingly. The maximum adsorption for 150 $\mu$ m and 250 $\mu$ m were at 80<sup>th</sup> and 40<sup>th</sup> minutes, respectively (54.895mg/l and 58.874mg/l). Kinetic modeling of the results of Cadmium (II) ion of both pore sizes were also investigated, reported and analysed. These results showed that Pseudo second order kinetic model best described the sorption process. The Mechanism of sorption showed that CMSH 150 $\mu$ m and 250 $\mu$ m, respectively were particle diffusion controlled. This will serve as parameters to consider in the design of treatment plants for heavy metal detoxification using biosorbents of different pore sizes.*

**Keywords:** Biosorbents, Detoxification, Heavy metals, Adsorption kinetics, Sorption mechanisms, Thiolation.

### Contribution/ Originality

This study is one of the very few studies which have investigated on Sorghum Hull and its use in the adsorption of Cadmium (II) ion from aqueous solution (synthetic wastewater). It documents the kinetics and mechanism of adsorption process; design pattern for wastewater treatment plant construction using a novel adsorbent.

## 1. INTRODUCTION

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 [1].

Adsorption, an established industrial separation technique used in bulk separation technique that uses both bulk/batch separation and purification has been proven to be one of the techniques

in heavy metal ion removal. Due to high cost of adsorbents purchasing and regeneration, and to accomplish the need of heavy metal ion removal, biosorption process has been developed. Biosorption is a new direction that points to the development of adsorbents of a combined and hybrid nature such as organic and inorganic materials [1]. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown high levels of adsorption being referred to as biosorbents commercially and for further research. Examples of such biomass materials includes Maize cob [2] modified Saw dust of Spruce [3].

## 2. CADMIUM

Cadmium is listed as a heavy metal; it occurs as a minor component in most zinc ores and therefore is a byproduct of zinc production. It was used for a long time as a pigment and for corrosion-resistant plating on steel, whereas cadmium compounds were used to stabilize plastic. The use of cadmium is generally decreasing due to its toxicity (it is specifically listed in the European Restriction of Hazardous Substances [4].

The most dangerous form of occupational exposure to cadmium is inhalation of fine dust and fumes, or ingestion of highly soluble cadmium compound [4]. Build-up of cadmium levels in the water, air, and soil has been occurring particularly in industrial areas. Acute exposure to cadmium fumes may cause flu like symptoms including chills, fever, and muscle ache sometimes referred to as "the cadmium blues." Symptoms may resolve after a week if there is no respiratory damage. It increases lipid per oxidation, in addition it depletes antioxidants, glutathione and protein-bound sulfhydryl groups.

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

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. Studies on the kinetics of metal sorption by various adsorbents are of importance for designing an adsorption system.

## 3. MATERIALS AND METHODS

### 3.1. Materials

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. Other materials used were Whatman No. 41 filter paper, glass wares and flasks.

### 3.2. Methods

#### 3.2a. Adsorbent Preparation

The Sorghum Hulls were washed and air dried for the metal ion sorption 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 $\mu$ m and 250 $\mu$ m [1].

#### 3.2b. Activation of Sorghum Hulls

The fine screened Sorghum Hulls powder was soaked in excess of 3.0M HNO<sub>3</sub> solution for 24 hours. This was then filtered through a Whatman No.41 Filter paper and rinsed with deionized water. The rinsed Sorghum Hulls were later air dried for 24 hours. The treatment of the biomass with 3.0M HNO<sub>3</sub> 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 [1].

#### 3.2c. Carbonization of the Sorghum Hulls

The carbonization process was conducted 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.

#### 3.2d. Chemical Modification of Sorghum Hulls with Mercapto-Acetic Acid (MAA)

The method was carried out according to [Imaga and Abia \[1\]](#). The air-dried, activated and carbonized Sorghum Hulls were acid treated with excess 1.0M Mercapto acetic acid (MAA)[HSCH<sub>2</sub>COOH] 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 $\mu$ m and 250 $\mu$ m. After 24 hours, the mixtures in the beakers designated as CMSH 150 $\mu$ m and 250 $\mu$ m were filtered off and air dried. The two working adsorbents CMSH 150 $\mu$ m and 250 $\mu$ m were stored in air tight plastic containers and labelled accordingly [1].

#### 3.2e. Preparation of Adsorbate Solutions for Sorption Studies

A stock solution of 1000ppm of the metal Cadmium was prepared from Cadmium Chloride CdCl<sub>2</sub> (dried); assay 95% (BDH laboratory reagent). Thereafter, serial dilution was carried out on the stock solution to obtain working solution of 60 ppm of the Cadmium (II) ion. The concentration of the standard was confirmed using an Atomic Adsorption Spectrophotometer. The pH of the solution was kept at 7.0.

### 3.2f. Sorption Studies at Different Contact Time

Kinetics of sorption for Cadmium (II) ion was carried out for each adsorbent (CMSH 150 $\mu$ m and 250 $\mu$ m) at pH of 7.0 and temperature of 28°C (301K). 30cm<sup>3</sup> of standard solution of the metal, initial concentration of 60mg/l was transferred into various 250cm<sup>3</sup> Erlenmeyer flask and labelled. Then 0.2g of each adsorbent CMSH 150 $\mu$ m and 250 $\mu$ 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 filtered. The residual concentration of metal ions in 20cm<sup>3</sup> 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 Cadmium (II) ion concentration was then calculated by difference. Glass wares and plastic wares were washed with deionized water and rinsed to eliminate errors [5].

## 4. RESULTS AND DISCUSSION

### 4.1. 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 Cadmium (II) ion adsorbed by the adsorbents CMSH 150 $\mu$ m and 250 $\mu$ 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 Cadmium (II) ion Adsorbed for CMSH 150 $\mu$ m and 250 $\mu$ m

Contact Time (MINS)	Amount of Metal Ion Concentration Adsorbed	
	Cd <sup>2+</sup> 150 $\mu$ m	Cd <sup>2+</sup> 250 $\mu$ m
20	54.713	54.912
40	54.687	58.874
60	54.874	54.894
80	54.895	54.986
100	54.753	54.864

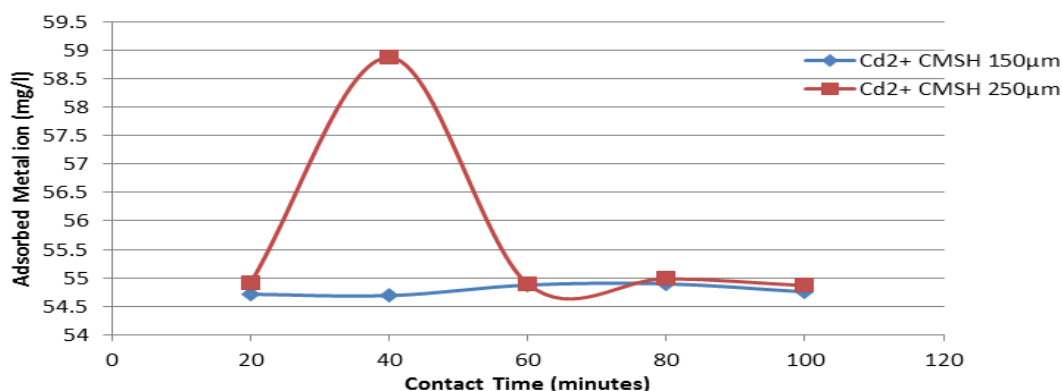


Fig-1. Graph of Amount Adsorbed versus Contact Time for Cd<sup>2+</sup> (CMSH 150 $\mu$ m and 250 $\mu$ m)

The maximum sorption time for 150 $\mu\text{m}$  and 250 $\mu\text{m}$  were at 80<sup>th</sup> and 40<sup>th</sup> minutes (54.895mg/l and 58.874mg/l), respectively. The Cadmium (II) ion sorption is higher in 250 $\mu\text{m}$  than in 150 $\mu\text{m}$ . The rate of sorption in 150 $\mu\text{m}$  occurred faster (20<sup>th</sup>, 40<sup>th</sup>, 60<sup>th</sup> and 100<sup>th</sup> minutes) [54.713, 54.687, 54.874, 54.753] mg/l than in 250 $\mu\text{m}$  (20<sup>th</sup>, 60<sup>th</sup>, 80<sup>th</sup> and 100<sup>th</sup> minutes) [54.912, 54.894, 54.986, 54.864] mg/l, respectively. 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. However, the sorption of Cadmium (II) ion by both 150 $\mu\text{m}$  and 250 $\mu\text{m}$  were very high.

#### 4.2. Kinetic Modeling

The kinetic models- Elovich, Pseudo first and Second order models were employed to investigate the kinetics of sorption of the divalent Cadmium (II) ion by the adsorbents.

##### 4.2a. 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 of Cadmium (II) ion 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.

##### 4.2b. 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  $q_t=q_t$ , 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 can be linearized in the 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 [6].

The pseudo-second order rate equation was tested for the sorption of Cadmium (II) ion on CMSH 150 $\mu$ m and 250 $\mu$ m, respectively. Table 2 presents data for the pseudo-second order constants. The variation of  $t/q_t$  with time from the pseudo-second order equation fits the adsorption of the Cadmium (II) ion by the adsorbents are shown in figures 2 and 3.

Table-2. Pseudo Second Order Constants for CMSH 150 $\mu$ m and 250 $\mu$ m

Constants	Cadmium (II) ion	
	CMSH 150 $\mu$ m	CMSH 250 $\mu$ m
R <sup>2</sup>	1.0000	0.9988
K <sub>2</sub> (gmg <sup>-1</sup> min <sup>-1</sup> )	4.107	0.092
h <sub>o</sub> (mgg <sup>-1</sup> min <sup>-1</sup> )	277.778	6.042
q <sub>e</sub> (mgg <sup>-1</sup> )	8.224	8.124

The results obtained showed very highly significant linear relationship of the sorbed Cadmium (II) ion by the various adsorbents CMSH 150 $\mu$ m and CMSH 250 $\mu$ m, respectively. The correlation coefficient (R<sup>2</sup>) values are high showing that pseudo second order model gave the best fit and a good description of Cadmium (II) ion sorption by the two adsorbents.

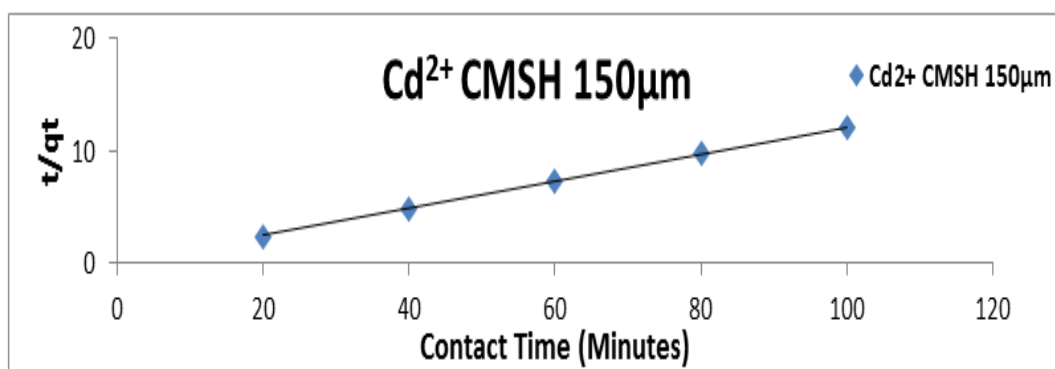


Fig-2. Pseudo Second Order Isotherm Model of Cd<sup>2+</sup> CMSH 150 $\mu$ m

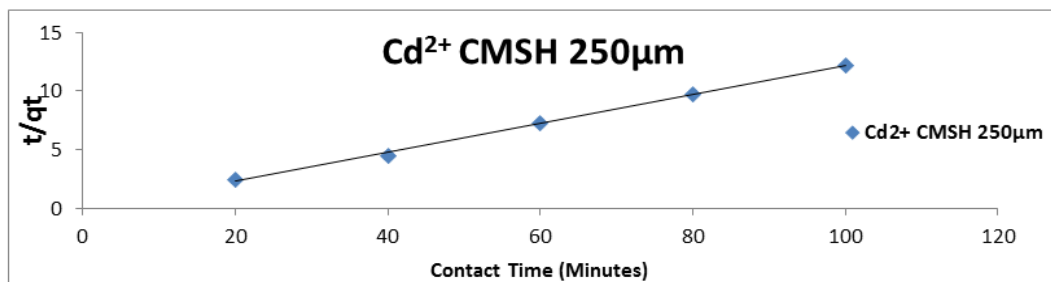


Fig-3. Pseudo Second Order Isotherm Model of Cd<sup>2+</sup> CMSH 250µm

#### 4.2c. 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 [1]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation given below [7]:

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

Where  $\alpha$  is the initial adsorption rate (mg/g min), and the parameter  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The initial adsorption rate,  $\alpha$ , and desorption constant,  $\beta$ , were calculated from the intercept and slope of the straight-line plots of  $q_t$  against  $\ln t$ . 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  $\alpha$  and  $\beta$  varied as a function of the solution temperature. Also, the experimental data did not give a good correlation for these results. The values of Elovich constants are shown in Table 3 below.

Table-3. Calculated Values of Elovich Isotherm Model Constants of Adsorbents 150µm and 250µm

Constants	Cd <sup>2+</sup> 150 µm	Cd <sup>2+</sup> 250 µm
R <sup>2</sup>	0.3092	0.0542
B(gmg <sup>-1</sup> )	81.301	10.267
$\alpha$ (mgg <sup>-1</sup> min <sup>-1</sup> )	3.296e+286	9.186e+37

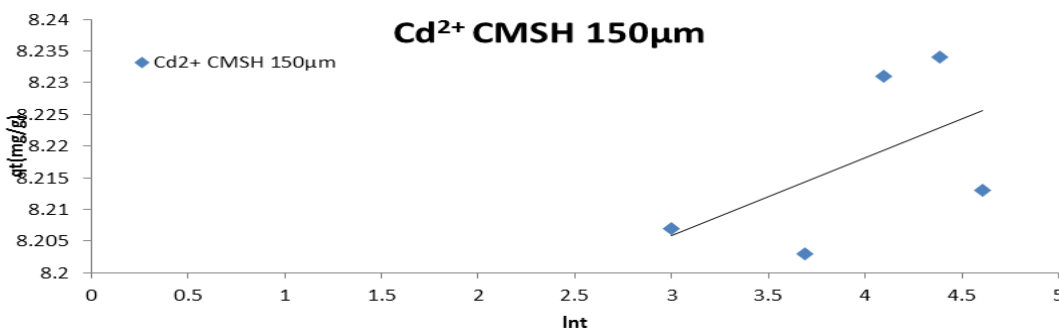
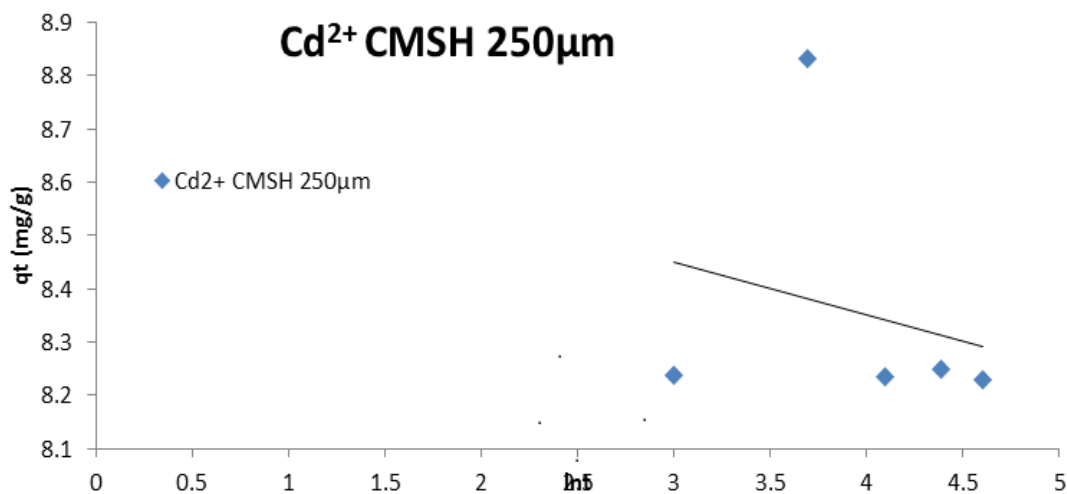


Fig-4. Elovich Isotherm Model of Cd<sup>2+</sup> CMSH 150µm

Fig-5. Elovich Isotherm Model of Cd<sup>2+</sup> CMSH 250µm

### 4.3. Sorption Mechanisms

#### 4.3a. Liquid Film Diffusivity Model

The kinetics of sorption of Cadmium (II) ion onto adsorbent of two 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 *et al.*, 2014 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 ( $\text{min}^{-1}$ ) 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 [1]. The diffusion of Cadmium (II) ions to the adsorbent surface is independent of the initial concentration of the Cadmium (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 [1]. 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. 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 [8].

Table-4. Liquid Film Diffusivity Constants for CMSH 150µm and 250µm

Constants	Cd <sup>2+</sup> 150 µm	Cd <sup>2+</sup> 250 µm
R <sup>2</sup>	0.9513	0.8718
K <sub>p</sub> (min <sup>-1</sup> )	30x10 <sup>-5</sup>	30x10 <sup>-5</sup>
D <sub>F</sub>	-0.0868	-0.0945



The  $R^2$  values of Cadmium (II) ion (CMSH 150 $\mu\text{m}$  and 250 $\mu\text{m}$ ) were relatively high suggesting that the diffusivity model does entirely support the sorption of Cadmium (II) ion using the adsorbent 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 Cadmium (II) ion (CMSH 150 $\mu\text{m}$  and 250 $\mu\text{m}$ ) are particle diffusion controlled since the plotted graphs are linear. Since sorption of Cadmium (II) ion of same adsorbent with two different pore sizes are 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 [9]; (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 [9]. This means that in the presence of a mixture of the metal ions, the metal ions compete for the adsorption sites on the adsorbent [1]. This competition affects the diffusion properties of the metal ions, hence decreases the adsorption capacity of the metal ions [1]. 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 metal ions for adsorption sites clearly affected the adsorption capacity [1, 9].

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 conclusion was also arrived at by Abia and Asuquo [10] in their study on  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cr}^{3+}$  with oil palm fibre.

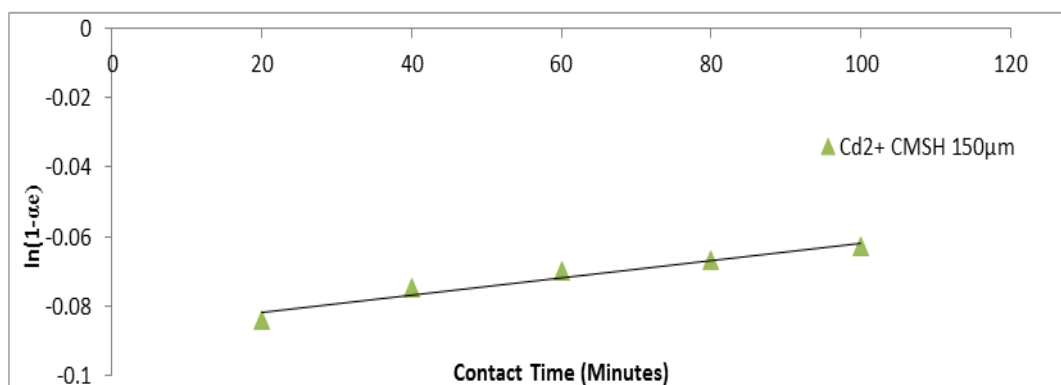


Fig-6. Liquid Film Diffusivity Model for CMSH 250 $\mu\text{m}$

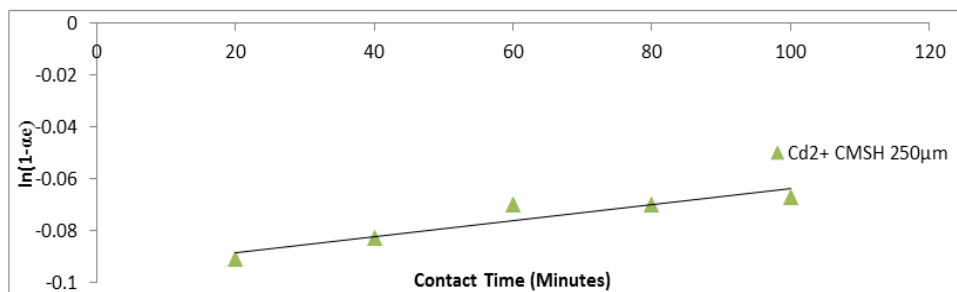


Fig-7. Liquid Film Diffusivity Model for CSMH 150µm

#### 4.3b. Mass Transfer Model

The mass transfer kinetic model is generally expressed as [Imaga and Abia \[1\]](#)

$$C_o - C_t = D \exp(K_o t) \tag{10}$$

Where,

$C_o$  = Initial metal ion concentration (mg/l)

$C_t$  = Metal ion concentration at time t in mg/l

T = Shaking time in minutes

D = Fitting diameter

$K_o$  = Constant which is the mass transfer adsorption coefficient

In a linear form, the equation in [10] above can be expressed thus:

$$\ln(C_o - C_t) = \ln D + K_o t \tag{11}$$

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  $\ln D$  and  $K_o$  can be determined from the intercept and slope of the plot, respectively [1].

Table-5: Mass Transfer Constants for CSMH 150µm and 250µm

Constants	Cd <sup>2+</sup> 150 µm	Cd <sup>2+</sup> 250 µm
R <sup>2</sup>	0.2184	0.1256
D	5.299	2.391
$K_o$	-0.0003	0.0076

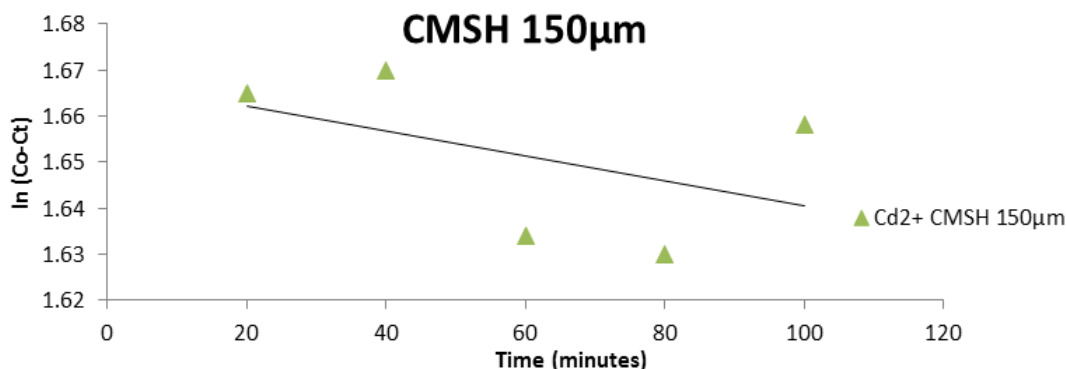
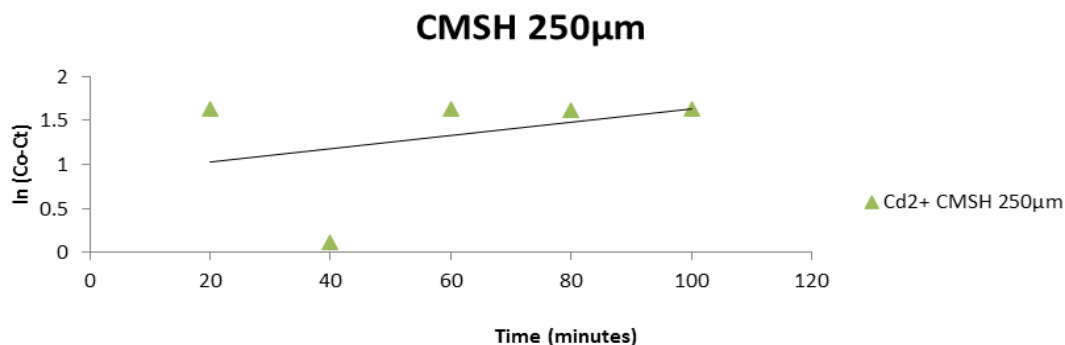


Fig-8. Mass Transfer Model of Metal Ions of Sample Pore Size CSMH 150µm



**Fig-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 adsorbent and its two pore sizes [1]. Mass transfer is the movement of chemical species in a fluid mixture caused by some forms of driving force. The two main mechanisms (diffusion and mass transport by convection) were not supported suggesting that mass transfer model does not favour the sorption of Cadmium (II) ion. 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. Their very low  $R^2$  values confirm this. Aikpokpodion, et al. [11] 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.

#### 4.3c. Intra Particle Diffusivity Model

Intra particle diffusivity equation for description of sorption kinetics was explored using the intra-particle diffusivity model given below [1]:

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

Where,

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

$C$  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 Diffusivity Constants for CMSH 150 $\mu$ m and 250 $\mu$ m

Constants	Cd <sup>2+</sup> 150 $\mu$ m	Cd <sup>2+</sup> 250 $\mu$ m
$R^2$	0.2773	0.0914
$K_{id}(\text{mgg}^{-1}\text{min}^{-1(1/2)})$	$2.29 \times 10^{-2}$	$-2.461 \times 10^{-1}$
$C$	54.613	57.551

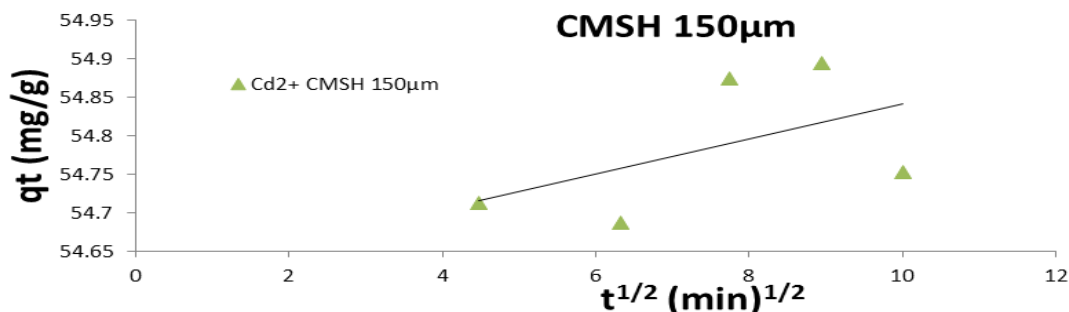


Fig-10. Intra Particle Diffusivity Model for CMSH 150µm

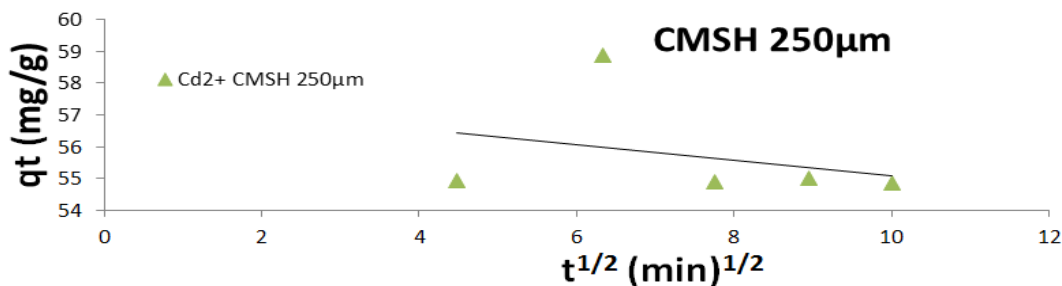


Fig-11. Intra Particle Diffusivity Model for CMSH 250µm

According to [Imaga and Abia \[1\]](#) 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 [\[1\]](#). 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 [\[1\]](#). 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 sorption of Cadmium (II) ion with the adsorbent of the two different pore sizes.

#### 4.3d. Intra Particle Diffusion Model

The intra particle diffusion model [\[10\]](#) is expressed as:

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

In linear form, the equation becomes

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

Where,

R = Percentage of metal ion adsorbed

t = Contact time in minutes

a = 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 Aikpokpodion, et al. [11] 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  $\text{Mg}^{2+}$  onto the studied soils.

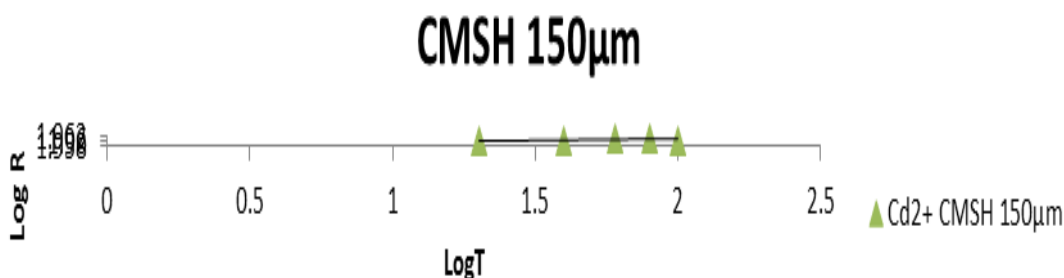


Fig-13. Intra Particle Diffusion Model for CMSH 150µm

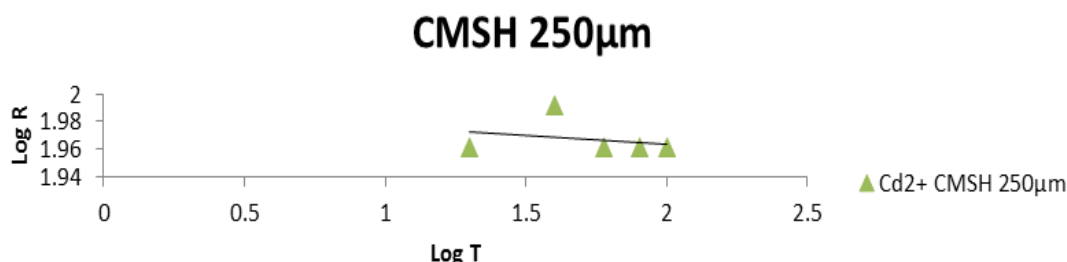


Fig-14. Intra Particle Diffusion Model for CMSH 250µm

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 any way favour the adsorption of Cadmium (II) ion 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 [8].

Table-7: Intra Particle Diffusion Constants for CMSH 150 $\mu\text{m}$  and 250 $\mu\text{m}$ 

Constants	Cd <sup>2+</sup> 150 $\mu\text{m}$	Cd <sup>2+</sup> 250 $\mu\text{m}$
R <sup>2</sup>	0.1674	0.3244
a	8 x 10 <sup>-4</sup>	1.1 x 10 <sup>-3</sup>
K <sub>id</sub> (mgg <sup>-1</sup> min <sup>-1(1/2)</sup> )	0.2920	0.2926

#### 4.4. Pore Size Analysis of Cadmium (II) Ion

Pore size is defined as the ability of the analyte molecules to penetrate inside the particle and interact with its inner 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 [12].

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 Cadmium (II) ion from aqueous solution.

### 5. 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 Cadmium (II) ion
- (ii) The result obtained can be used for various design purposes.
- (iii) These results can be used as a basis for the study of desorption and recovery of Cadmium (II) ion from solution.
- (iv) Pore size analysis showed that 150 $\mu\text{m}$  mesh had faster adsorption rate than 250 $\mu\text{m}$  mesh, although both recorded high adsorption values.
- (v) For liquid film diffusivity model, Cadmium (II) ion (CMSH 150 $\mu\text{m}$  and 250 $\mu\text{m}$ ) favoured particle diffusion controlled sorption.
- (vi) Mass transfer, Intra particle diffusivity, Intra particle diffusion and Elovich models did not favour the sorption of Cadmium (II) ion using the adsorbent of the two different pore sizes.

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