



**Adsorption kinetics and mechanisms of nickel (II) ion sorption using carbonized unmodified sorghum (*Sorghum bicolor*) hull of two pore sizes (150 $\mu$ m and 250 $\mu$ m)**

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**ABSTRACT**

Aim of this study was to investigate the use of unmodified and carbonized Sorghum Hull (CUSH 150 $\mu$ m and 250 $\mu$ m) in the removal of Nickel (II) ion from aqueous solution. The effect of contact time was investigated and reported. The maximum adsorption for 150 $\mu$ m and 250 $\mu$ m were at 40<sup>th</sup> and 60<sup>th</sup> minutes respectively (38.254mg/l and 38.545mg/l). Both pore sizes showed peak adsorption of Ni<sup>2+</sup> at different adsorption time respectively. Kinetic modelling of the results of Ni<sup>2+</sup> of both pore sizes were also investigated. These results showed that Pseudo second order kinetic model best describes the process and the Mechanism of adsorption show that both 150 $\mu$ m and 250 $\mu$ m were film 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, pore size, thiolation, biosorption, carbonized unmodified sorghum hull (CUSH).

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**INTRODUCTION**

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 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.

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 often be 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.

## Nickel

It is found in all soils and is emitted from volcanoes. Pure nickel is a hard, silvery-white metal that is combined with other metals to form alloys. Some of the metals that nickel can be alloyed with are iron, copper, chromium, and zinc. These alloys are used in the making of metal coins and jewelry and in industry for making metal items. Nickel and its compounds have no characteristic odor or taste. Nickel is required to maintain health in animals. A small amount of nickel is probably essential for humans, although a lack of nickel has not been found to affect the health of humans. Nickel compounds are also used for nickel plating, to color ceramics, to make some batteries, and as catalysts that increase the rate of chemical reactions. Major sources of exposure are: tobacco smoke, auto exhaust, fertilizers, superphosphate, food processing, hydrogenated-fats-oils, industrial waste, stainless steel cookware, testing of nuclear devices, tobacco smoke, baking powder, combustion of fuel oil, dental work and bridges. Acute toxic effects occur in two stages, immediate and delayed. Headache, dizziness, shortness of breath, vomiting, and nausea are the initial symptoms of overexposure; the delayed effects (10 to 36 h) consist of chest pain, coughing, shortness of breath, bluish discoloration of the skin, and in severe cases, delirium, convulsions, and death.

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, Sorghum Hull (*sorghum bicolor*) was used as biosorbent in the removal of heavy metal Ni<sup>2+</sup> 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 will be investigated.

## EXPERIMENTAL SECTION

### 2.1 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.

### 3.0 Methods

#### 3.1 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 150µm and 250µm.

#### 3.2 Activation of Sorghum Hulls

The screened fine Sorghum Hulls powder was further soaked in excess of 3.0M HNO<sub>3</sub> 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<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.

##### 3.2.1 Carbonisation of 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.

##### 3.2.2 Preparation of Adsorbate Solutions for Sorption Studies

A stock solution of 1000ppm of the metal Nickel was prepared from Nickel Acetate (C<sub>4</sub>H<sub>6</sub>NiO<sub>4</sub> or Ni(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>); assay 99% (BDH laboratory reagent). 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.

**3.2.3 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 Ni<sup>2+</sup> was carried out for each adsorbent (CUSH 150µm and 250µm) 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 CUSH 150µm and 250µm 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 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 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).

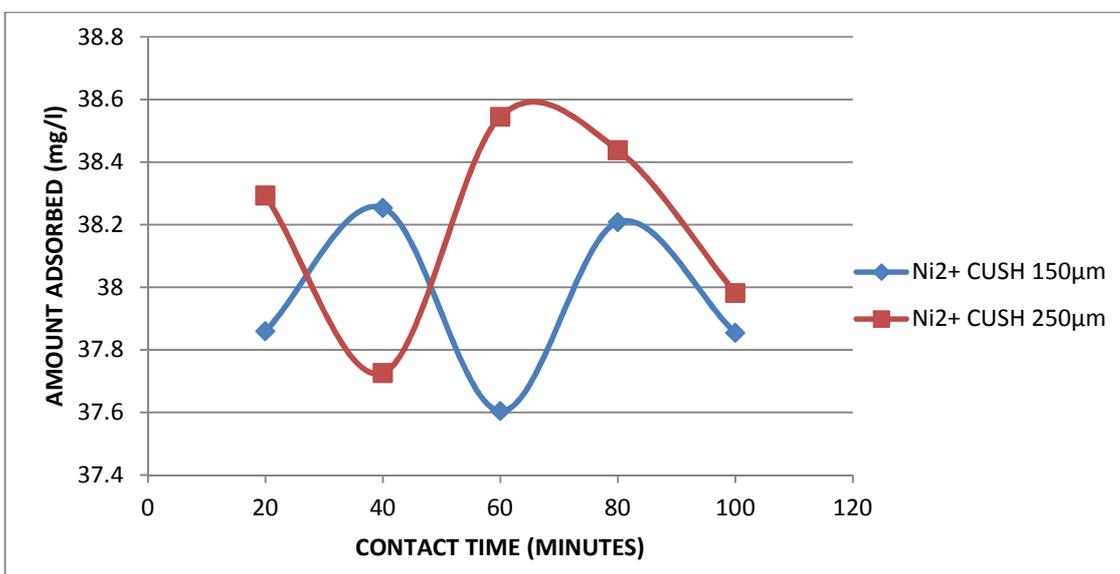
**RESULTS AND DISCUSSION**

**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 Ni<sup>2+</sup> adsorbed by the adsorbents CUSH 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 figure 1.

**TABLE 1: Effect of contact time on amount of metal ion concentration adsorbed for CUSH 150µm and 250µm**

CONTACT TIME(MINS)	Amount of Metal ion concentration adsorbed	
	Ni <sup>2+</sup> 150µm	Ni <sup>2+</sup> 250µm
20	37.859	38.293
40	38.254	37.726
60	37.604	38.545
80	38.208	38.438
100	37.854	37.982



**Fig 1: Graph of Amount Adsorbed versus Contact Time for Ni<sup>2+</sup> (CUSH 150µm and 250µm)**

The maximum adsorption time for 150µm and 250µm were at 40<sup>th</sup> and 60<sup>th</sup> minutes (38.254mg/l and 38.545mg/l), respectively. The rate of adsorption in 250µm occurred faster (20<sup>th</sup>, 60<sup>th</sup>, 80<sup>th</sup> and 100<sup>th</sup> minutes) [38.293, 38.545,

38.438 and 37.982]mg/l than in 150µm except in the 40<sup>th</sup> minute where the adsorption of Ni<sup>2+</sup> was higher in 150µm than in 250µm. This could be attributed to the non-chemical modification of the two pore sizes of the adsorbent.

#### 4.2 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.

##### 4.2.1 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.

##### 4.2.2 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 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 Ni<sup>2+</sup> ion on CUSH 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 the metal ion by the adsorbents is shown in figures 2 and 3.

Table 2: Pseudo Second Order constants for CUSH 150µm and 250µm

CONSTANTS	Nickel (II) ion	
	CUSH 150µm	CUSH 250µm
R <sup>2</sup>	<b>0.9998</b>	<b>0.9997</b>
K <sub>2</sub> (gmg <sup>-1</sup> min <sup>-1</sup> )	2.972	2.244
h <sub>0</sub> (mgg <sup>-1</sup> min <sup>-1</sup> )	96.154	73.529
q <sub>e</sub> (mgg <sup>-1</sup> )	5.688	5.724

The results obtained show a highly significant linear relationship of the sorbed ion by the various adsorbents. The correlation coefficient (R<sup>2</sup>) values are high(0.9998and 0.9997) showing that pseudo second order model gave the best fit and describes the adsorption of the Nickel(II) ion of the two adsorbents.

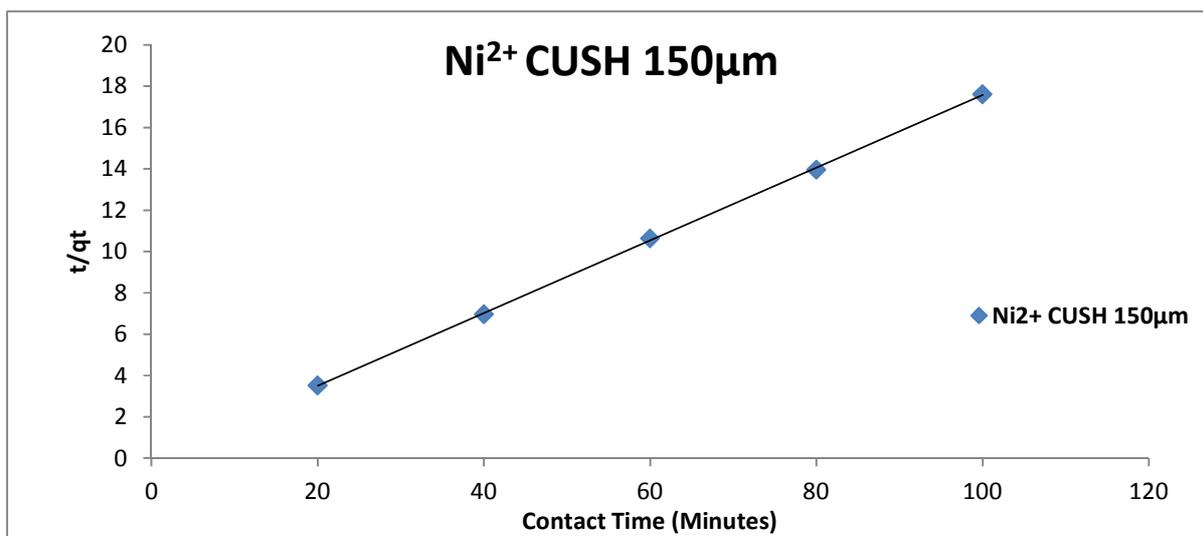


Fig 2 Pseudo Second Order Isotherm Model of Ni<sup>2+</sup> CUSH 150µm

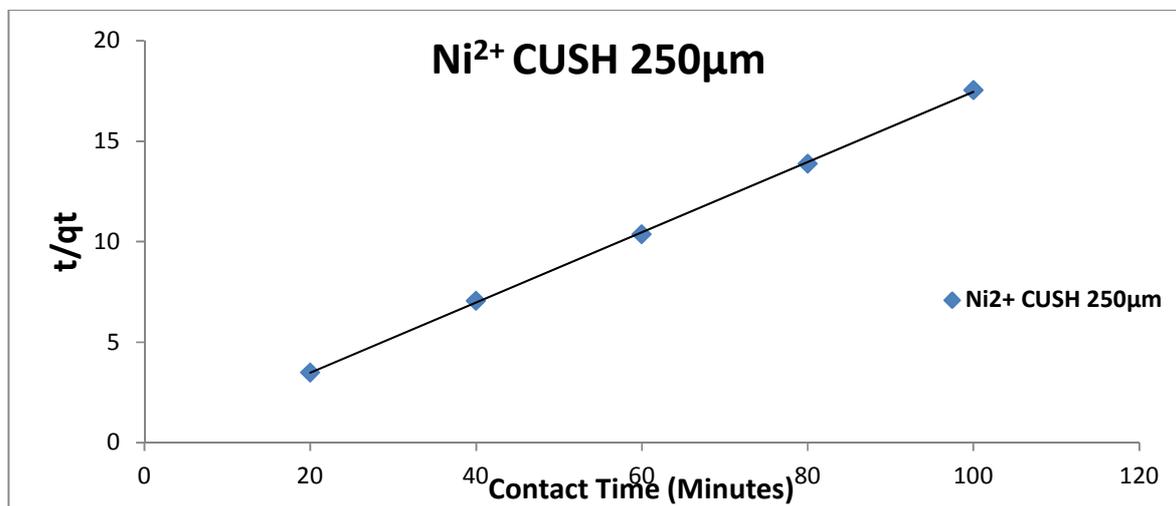


Fig 3 Pseudo Second Order Isotherm Model of Ni<sup>2+</sup> CUSH 250µm

4.2.3 Elovich Isotherm Model

Elovich model equation was also used successfully to describe thesecond 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):

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

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 Elovich coefficients could be computed from the plots  $q_t$  versus  $\ln t$ . 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  $\ln t$ . 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  $\alpha$  and  $\beta$  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 150 $\mu$ m and 250 $\mu$ m

CONSTANTS	Ni <sup>2+</sup> 150 $\mu$ m	Ni <sup>2+</sup> 250 $\mu$ m
R <sup>2</sup>	5E-05	0.0026
B(gmg <sup>-1</sup> )	2500	243.902
$\alpha$ (mgg <sup>-1</sup> min <sup>-1</sup> )	1.936e+6176	6.419e+602

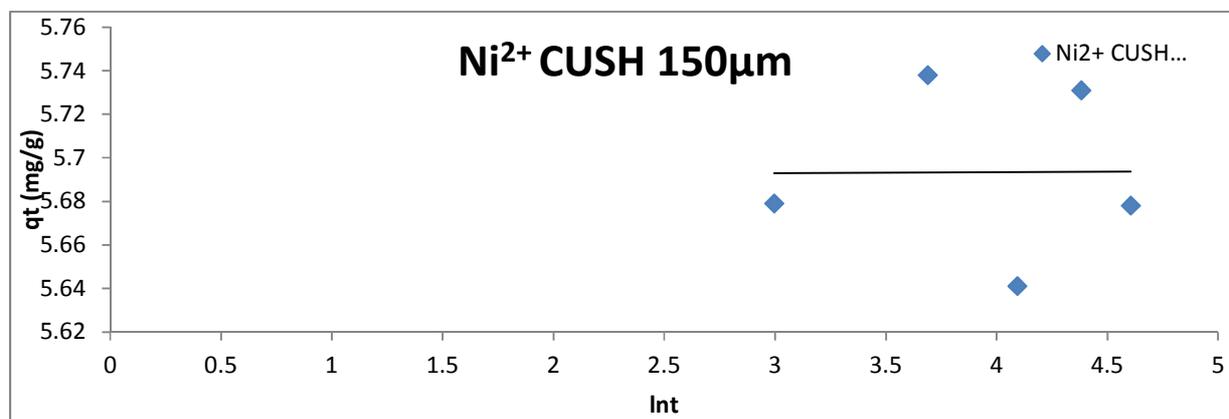


Fig 4 Elovich Isotherm Model of Ni<sup>2+</sup> CUSH 150 $\mu$ m

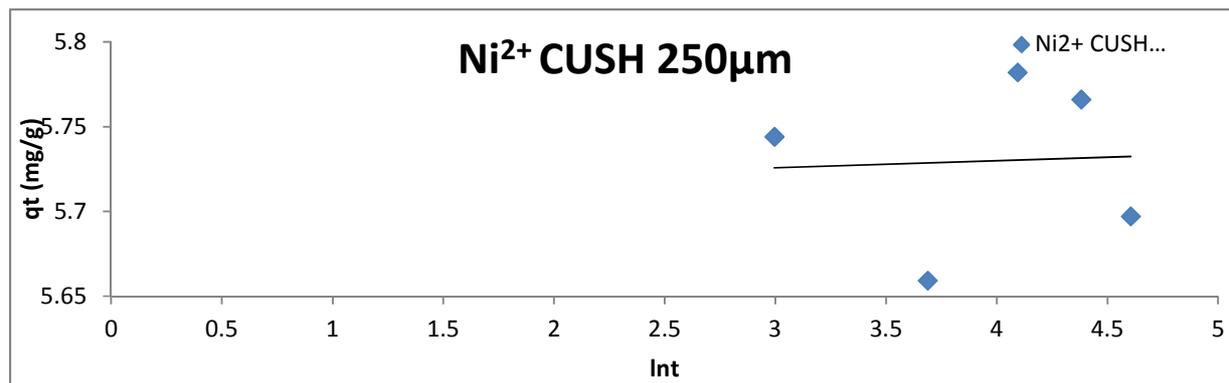


Fig 5 Elovich Isotherm Model of Ni<sup>2+</sup> CUSH 250 $\mu$ m

### 4.3 Adsorption Mechanisms

#### 4.3.1 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:

$$\ln(1 - \alpha_e) = -K_p t + D_F \tag{9}$$

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 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 CUSH 150 $\mu\text{m}$  and 250 $\mu\text{m}$

CONSTANTS	Ni <sup>2+</sup> 150 $\mu\text{m}$	Ni <sup>2+</sup> 250 $\mu\text{m}$
R <sup>2</sup>	<b>0.6000</b>	<b>0.1073</b>
K <sub>p</sub> (min <sup>-1</sup> )	3x10 <sup>-5</sup>	60x10 <sup>-5</sup>
D <sub>F</sub>	-0.0258	-0.0625

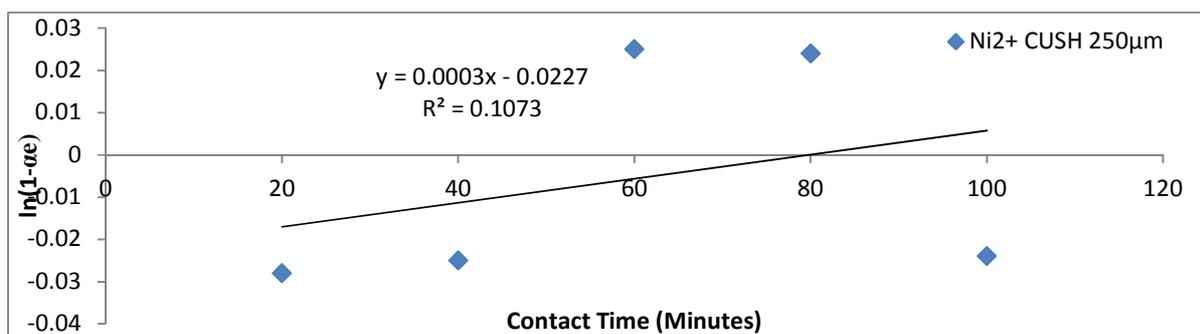


Fig 6 Liquid Film Diffusivity Model for CUSH 250 $\mu\text{m}$

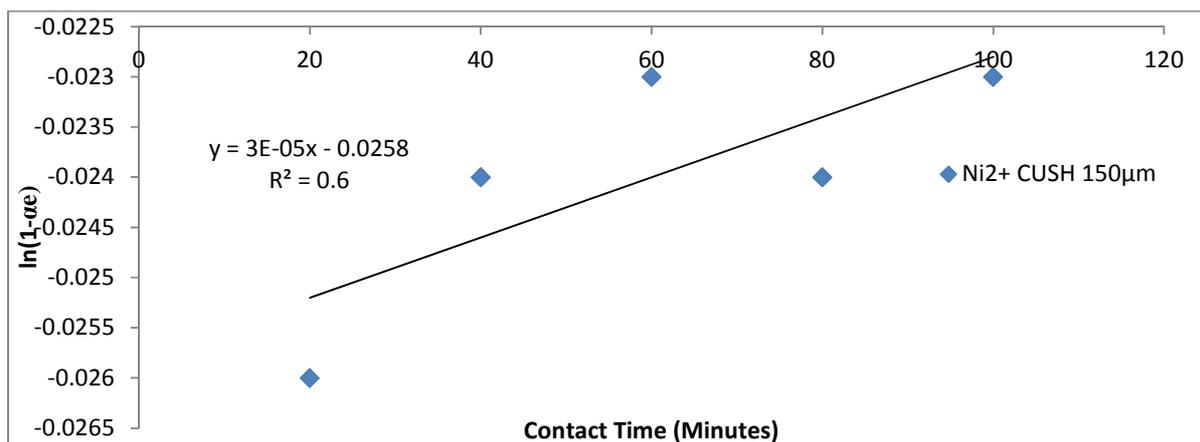


Fig 7 Liquid Film Diffusivity Model for CUSH 150 $\mu\text{m}$

The R<sup>2</sup> value of Ni<sup>2+</sup> 150 $\mu\text{m}$  and 250 $\mu\text{m}$  suggests that the diffusivity model does not entirely support the adsorption of Ni<sup>2+</sup> 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 Ni<sup>2+</sup> 150µm and 250µm is not a straight line describing Ni<sup>2+</sup> 150µm and 250µmas film diffusion controlled since the plotted graph is non- linear.

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<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and Cr<sup>3+</sup> with oil palm fibre.

**4.3.2 Mass Transfer Model**

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

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

Where,

C<sub>o</sub> is the initial metal ion concentration (mg/l)

C<sub>t</sub> is the metal ion concentration at time t in mg/l

T is the shaking time in minutes

D is the fitting diameter

K<sub>o</sub> is a constant which is the mass transfer adsorption coefficient

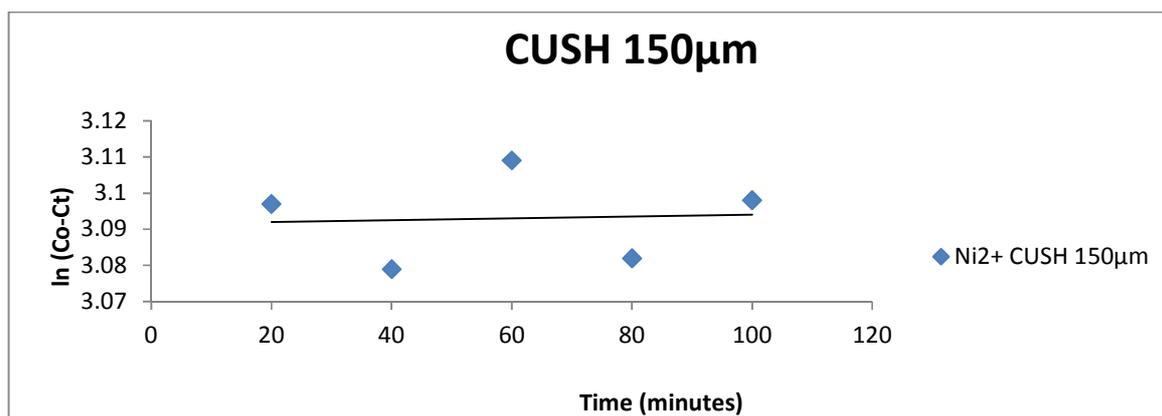
A linearized form of the equation is written thus:

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

If the sorption of the metal ion is depicted by the mass transfer model, then the plot of ln (C<sub>o</sub>-C<sub>t</sub>) versus time should give a linear relationship from where lnD and K<sub>o</sub> can be determined from the intercept and slope of the plot, respectively.

**Table 5: Mass Transfer Constants for CUSH 150µm and 250µm**

CONSTANTS	Ni <sup>2+</sup> 150 µm	Ni <sup>2+</sup> 250 µm
R <sup>2</sup>	<b>0.0041</b>	<b>0.0017</b>
D	22.010	21.828
K <sub>o</sub>	3E-05	-2E-05



**Fig 8 Mass Transfer Model of Ni<sup>2+</sup> CUSH 150µm**

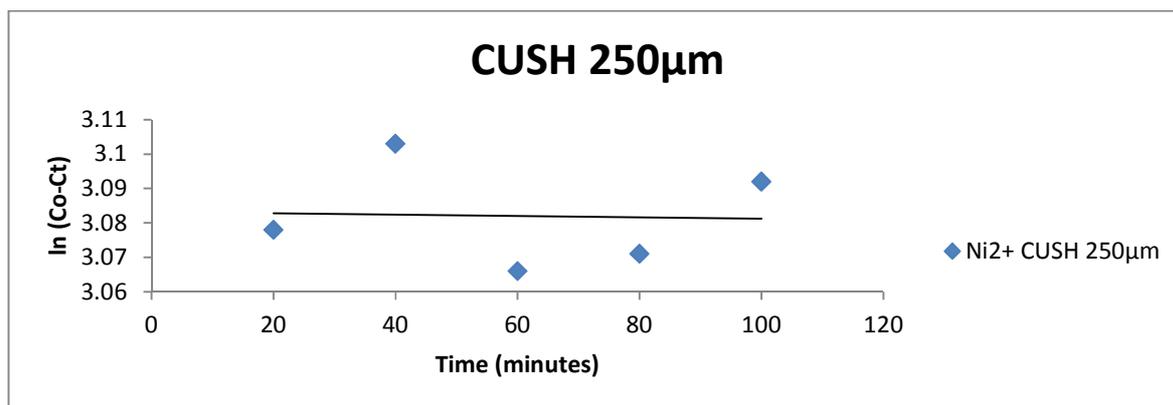


Fig 9 Mass Transfer Model of Ni<sup>2+</sup> CUSH 250µm

From the results, the low R<sup>2</sup> values suggest that the mass transfer diffusivity model does not support the adsorption of the metal ions using the adsorbent with its 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). These mechanisms (diffusion and mass transport by convection) were not supported suggesting that mass transfer model does not favour the sorption of Ni<sup>2+</sup>. The diffusion rate constant K<sub>o</sub> 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<sup>2</sup> 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.

#### 4.3.3 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):

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

Where,

k<sub>id</sub> is the rate of sorption controlled by intra particle diffusivity (mgg<sup>-1</sup>min<sup>-1(1/2)</sup>)

C depicts the boundary layer thickness.

This model predicts that the plot of q<sub>t</sub> versus t<sup>1/2</sup> should be linear with k<sub>id</sub> 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 CUSH 150µm and 250µm

CONSTANTS	Ni <sup>2+</sup> 150 µm	Ni <sup>2+</sup> 250 µm
R <sup>2</sup>	0.0002	0.0029
K <sub>id</sub> (mgg <sup>-1</sup> min <sup>-1(1/2)</sup> )	-1.8 x 10 <sup>-3</sup>	8.4 x 10 <sup>-3</sup>
C	37.969	38.134

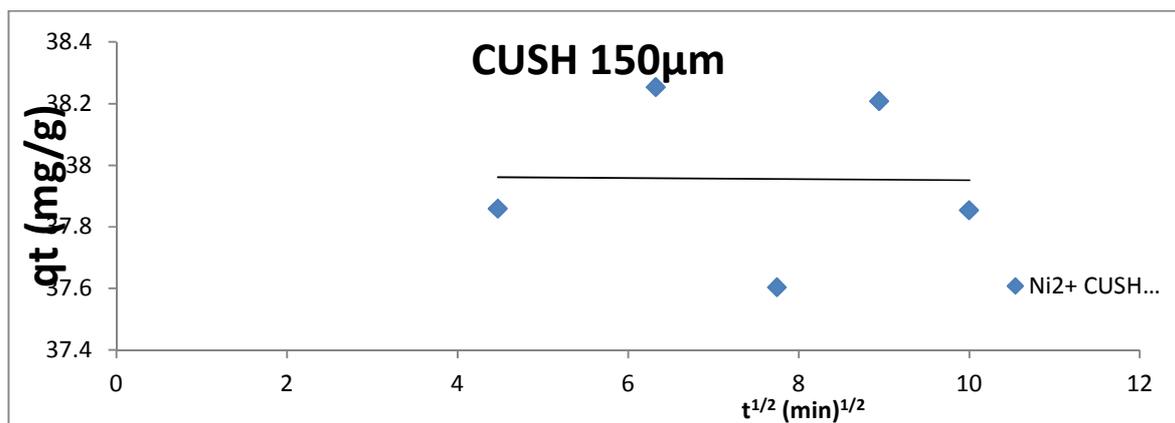


Fig10 Intra Particle Diffusivity Model for Ni<sup>2+</sup> CUSH 150µm

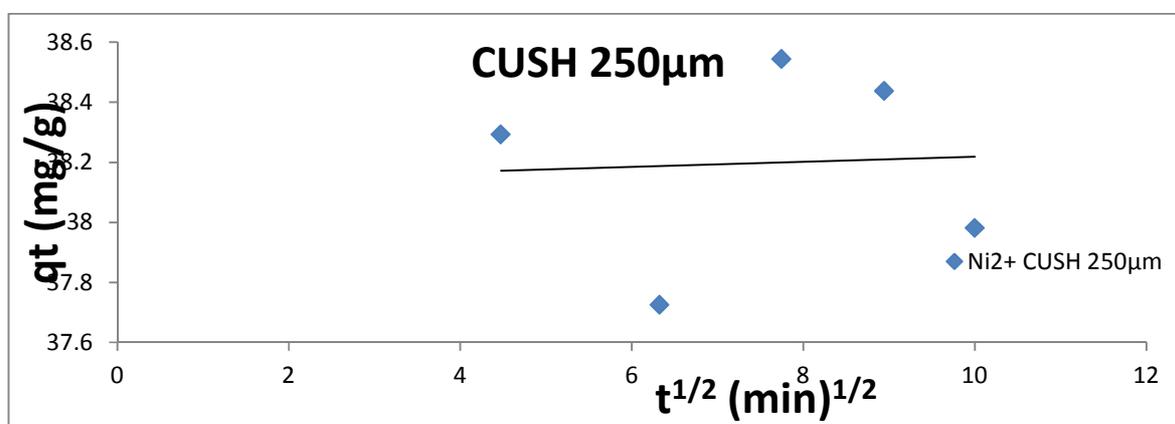


Fig 11 Intra Particle Diffusivity Model for Ni<sup>2+</sup> CUSH250µm

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

1. High R<sup>2</sup> values to ascertain applicability
2. Straight line which passes through the origin for the plot area q<sub>t</sub> versus t<sup>1/2</sup>
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<sub>id</sub> illustrate an enhancement rate of adsorption, whereas, larger k<sub>id</sub> 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<sub>id</sub> 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 Ni<sup>2+</sup> with the adsorbent of the two different pore sizes.

#### 4.3.4 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:

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

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

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  $\text{Mg}^{2+}$  onto the studied soils.

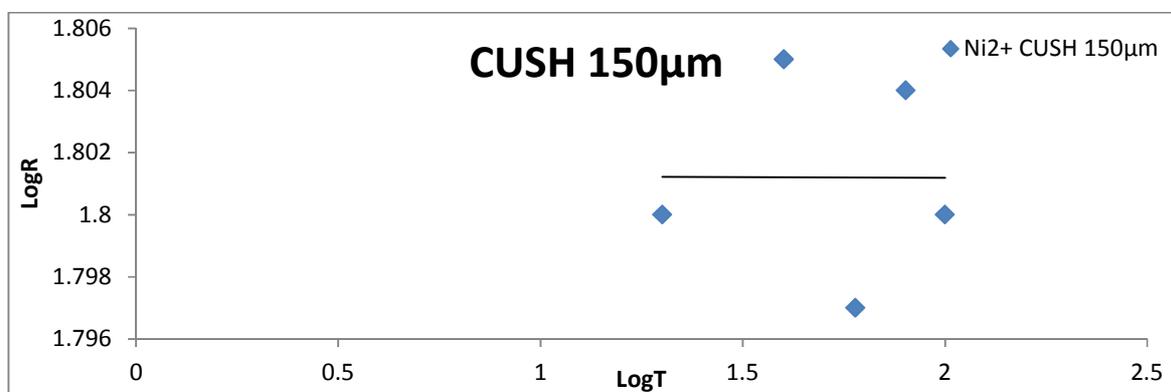


Fig 12 Intra Particle Diffusion Model for  $\text{Ni}^{2+}$  CUSH 150 $\mu\text{m}$

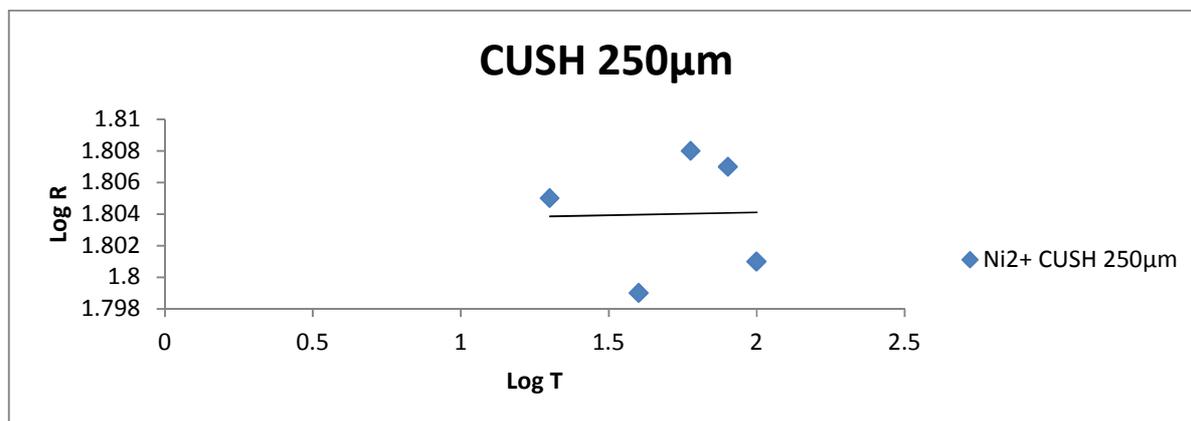


Fig 13 Intra Particle Diffusion Model for  $\text{Ni}^{2+}$  CUSH 250 $\mu\text{m}$

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 Nickel(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 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 CUSH 150µm and 250µm

CONSTANTS	Ni <sup>2+</sup> 150 µm	Ni <sup>2+</sup> 250 µm
R <sup>2</sup>	1E-05	0.0092
a	-4 x 10 <sup>-5</sup>	1.64 x 10 <sup>-2</sup>
K <sub>d</sub> (mgg <sup>-1</sup> min <sup>-1(1/2)</sup> )	0.2556	0.2441

#### 4.4 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 (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 Ni<sup>2+</sup> from aqueous solution.

#### CONCLUSION

The conclusions based on experimental study were:

- (i) Adsorbent preparation by carbonization and non-chemical modification of biosorbent showed good affinity for the metal ion Ni<sup>2+</sup>.
- (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 Nickel(II) ion from solution.
- (iv) Pore size analysis showed that 250µm mesh had faster adsorption rate than 150µm mesh except at the 40<sup>th</sup> minute, although both recorded high adsorption values.
- (v) For liquid film diffusivity model, Ni<sup>2+</sup> 150µm and 250µm both favour film diffusion controlled adsorption.
- (vi) Intraparticle diffusivity model, Intraparticle diffusion model, Mass transfer model, Pseudo first order model and Elovich model did not in any way favour the adsorption of Ni<sup>2+</sup> from solution.

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