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Adsorption kinetics and mechanisms of Ni^{2+} sorption using carbonized and modified sorghum (*Sorghum bicolor*) hull of two pore sizes (150 μm and 250 μm): A comparative study

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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 in the removal of Nickel (II) ion from aqueous solution. The effect of contact time was investigated and reported. The maximum adsorption for 150 μm and 250 μm were at the 80th minutes respectively (38.354 mg/l and 38.173 mg/l). Both pore sizes showed peak adsorption of Ni^{2+} at a same adsorption time. Kinetic modelling of the results of Ni^{2+} 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 film diffusion controlled was 150 μm and intraparticle diffusion control was 250 μm . 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.

1. Introduction

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. 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).

Recent environmental concerns as well as heightened defence against chemical terrorism call for both new protection technologies and for the improvement of existing ones including adsorption. Adsorption, an established industrial separation technique used in the bulk separation technique used both in 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 a modification for environmental application.

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

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

1.1 Nickel

Nickel is a very abundant element. In the environment, it is found primarily combined with oxygen (oxides) or sulfur (sulfides). 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

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alloys are used in the making of metal coins and jewelry and in industry for making metal items. 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. 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. 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. By breathing air or smoking tobacco containing nickel. 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. Recovery is protracted and characterized by fatigue on slight exertion. 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 Ni^{2+} 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.

2. 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.

2. Methods

2.1 Adsorbent Preparation

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

2.2 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.

2.2.1 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.

2.2.2 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 CSMH 150 μm and 250 μm .

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

2.2.3 Preparation of Adsorbate Solutions for Sorption Studies

A stock solution of 1000 ppm of the metal Nickel was prepared from Nickel Acetate ($\text{C}_4\text{H}_6\text{NiO}_4$ or $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$; 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.

2.2.4 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^{2+} was carried out for each adsorbent (CSMH 150 μm and 250 μm) at pH of 7.0 and temperature of 28 °C (301K). 30 cm^3 of standard solution of the metal, initial concentration of 60 mg/l was transferred into various 250 cm^3 Erlenmeyer flask and labelled. Then 0.2 g of each adsorbent CSMH 150 μm and 250 μm 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 20 cm^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).

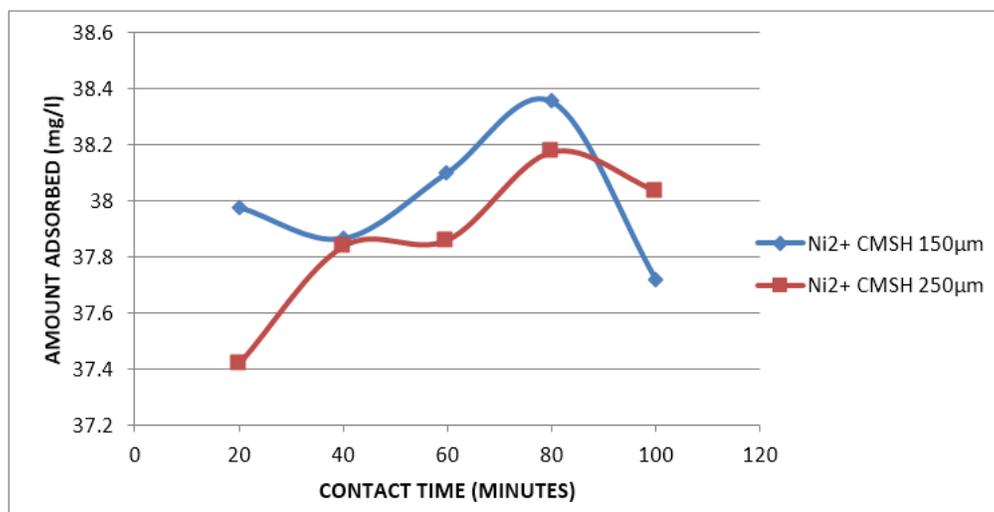
3. Results and Discussion

3.1 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^{2+} adsorbed by the adsorbents CSMH 150 μm and 250 μm as a function of time is presented in table 1. The variation in the amount of the metal ion adsorbed by the adsorbents is shown in figure 1.

Table 1: Effect of contact time on amount of metal ion concentration adsorbed for CMSH 150 μm and 250 μm

Contact Time(Mins)	Amount Of Metal Ion Concentration Adsorbed	
	Ni ²⁺ 150 μm	Ni ²⁺ 250 μm
20	37.979	37.418
40	37.867	37.837
60	38.102	37.860
80	38.354	38.173
100	37.719	38.034

**Fig 1:** Graph of Amount Adsorbed versus Contact Time for Ni²⁺ (CMSH 150 μm and 250 μm)

The maximum adsorption time for 150 μm and 250 μm were at the 80th minutes respectively (38.354 mg/l and 38.173 mg/l) but the Ni²⁺ adsorption is higher in 150 μm than in 250 μm except in the 100th minute. The rate of adsorption in 150 μm occurred faster (20th, 40th, 60th minute) [37.979, 37.867, 38.102] mg/l than in 250 μm (20th, 40th, 60th minutes) [37.418, 37.837, 37.860] mg/l, respectively except in the 100th minute where the adsorption of Ni²⁺ was higher in 250 μm than in 150 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 size gives slower rate of adsorption. The smaller pore size (150 μm) has larger surface area than the 250 μm which has a smaller surface area.

3.2 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.

3.2.1 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 $\text{gmg}^{-1} \cdot \text{min}^{-1}$

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.

3.2.2 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_0 can be regarded as the initial rate as $(t/q_t) \rightarrow 0$ hence h_0 (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^{2+} ion on CMSH 150 μm and 250 μm , 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 cmsH 150 μm and 250 μm

Constants	Nickel (II) Ion	
	CMSH 150 μm	CMSH 250 μm
R^2	0.9997	1.0000
$K_2(gmg^{-1}min^{-1})$	1.012	0.389
$h_o(mgg^{-1}min^{-1})$	32.680	12.788
$q_e(mgg^{-1})$	5.682	5.737

The results obtained show a highly significant linear relationship of the sorbed ion by the various adsorbents. The correlation coefficient (R^2) values are high (0.9997 to 1.0000) showing that pseudo second order model gave the best fit and describes the adsorption of the Nickel (II) ion of all the adsorbents.

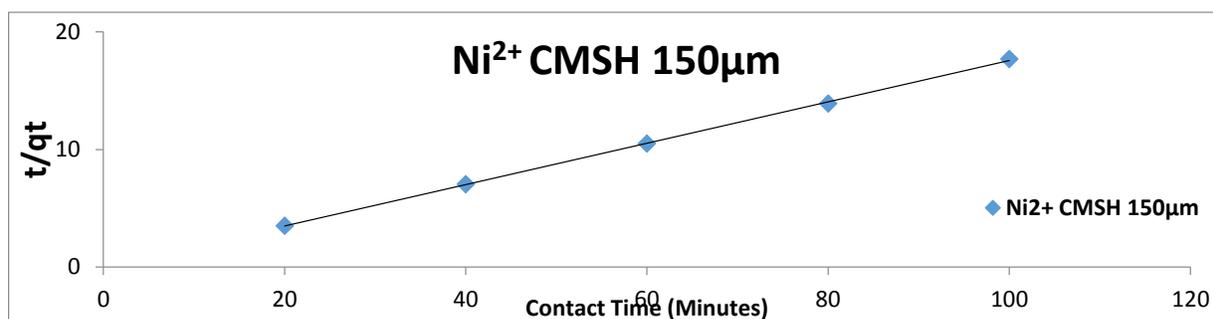


Fig 2: Pseudo Second Order Isotherm Model of Ni^{2+} CMSH 150 μm

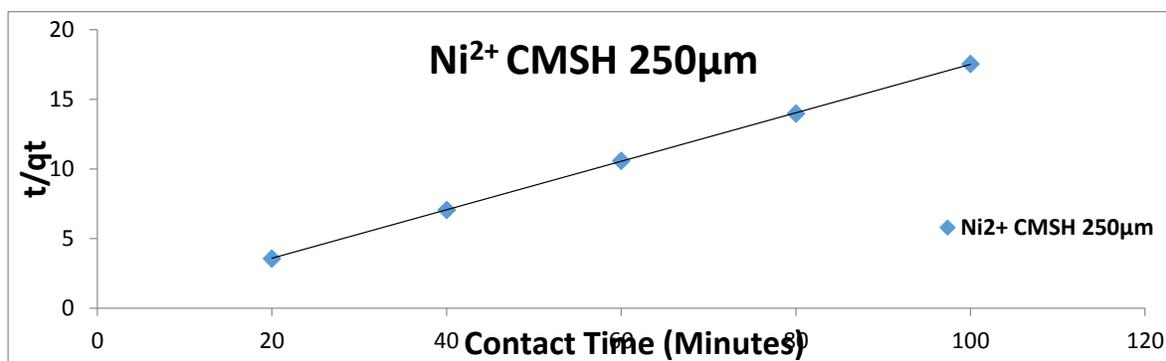


Fig 3: Pseudo Second Order Isotherm Model of Ni^{2+} CMSH 250 μm

3.2.3 Elovich Isotherm Model

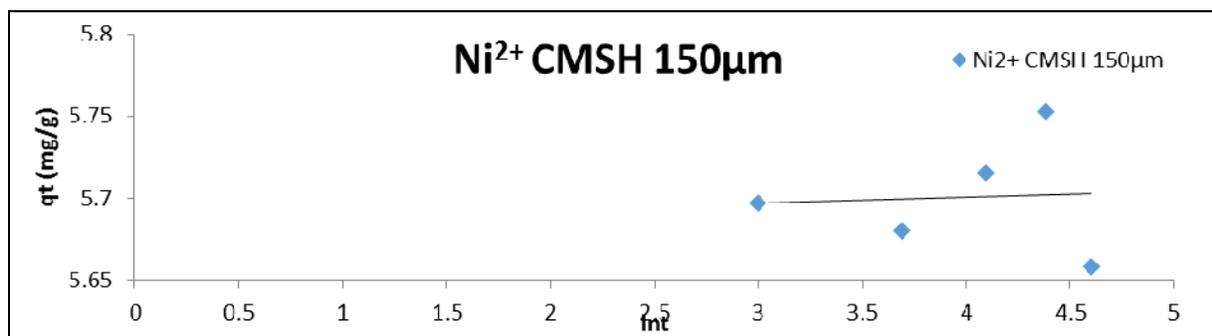
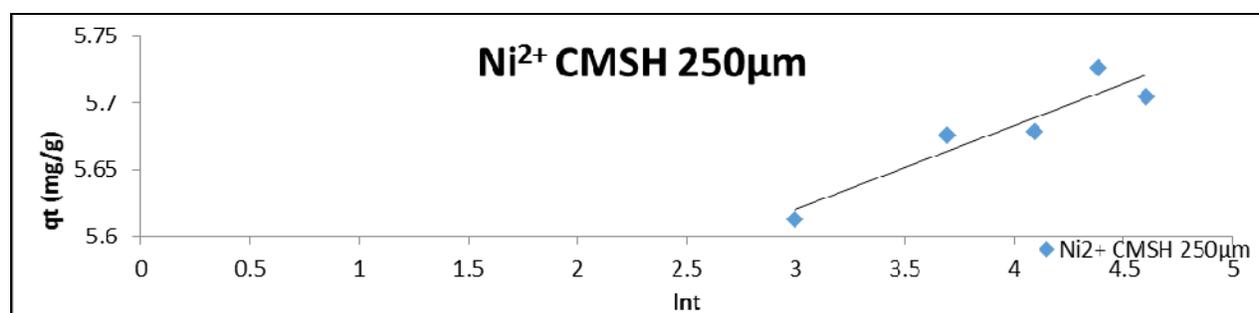
Elovich model equation was also used successfully to describe the second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent. It has extensively been accepted that the chemisorption process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

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

Where α is the initial adsorption rate (mg/g min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The Elovich coefficients could be computed from the plots q_t versus $\ln t$. The initial adsorption rate, α , and desorption constant, β , were calculated from the intercept and slope of the straight-line plots of q_t against $\ln t$. Table 3 lists the kinetic constants obtained from the Elovich equation. It will be seen that applicability of the simple Elovich equation for the present kinetic data indicates that the Elovich equation was unable to describe properly the kinetics of the metal ion on the adsorbents of the two pore sizes. The value of α and β varied as a function of the solution temperature. Also, the experimental data did not give a good correlation for these results.

Table 3: calculated values of elovich isotherm model constants of adsorbents 150 μm and 250 μm

Constants	Ni ²⁺ 150 μm	Ni ²⁺ 250 μm
R ²	0.0038	0.8730
B(gmg ⁻¹)	285.714	15.974
$\alpha(\text{mgg}^{-1}\text{min}^{-1})$	1.534e+703	3.046e+36

**Fig 4:** Elovich Isotherm Model of Ni²⁺ CSMH 150 μm **Fig 5:** Elovich Isotherm Model of Ni²⁺ CSMH 250 μm

3.3 Adsorption Mechanisms

3.3.1 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:

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

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

A plot of $\ln(1 - \alpha_e)$ versus time (t) yields the K_p the rate constant (min^{-1}) as the slope of the graph and a dimensionless constant D_F as intercept. If a plot of $\ln(1 - \alpha_e)$ against t is a straight line, then adsorption is controlled by particle diffusion and the diffusion of the metal ions to the adsorbent surface is independent of the initial concentration of the metal ions, if it is not a straight line, then it indicates that the sorption process is controlled by film-diffusion. The fractional attainment at equilibrium is the ratio of the amounts of sorbate removed from solution after a certain time to that removed when sorption equilibrium is attained. It would definitely be expected that factors such as the number of reactive sites on the substrate and the bulkiness of the substrate would affect the rate of sorption. However, a great deal of information is gotten from the fractional attainment of equilibrium. The rate of attainment of equilibrium may be either film diffusion controlled or particle-diffusion controlled, even though this

two different mechanism cannot be sharply demarcated (Itodo *et al.*, 2010).

Table 4: liquid film diffusivity constants for cmsh 150 μm and 250 μm

Constants	Ni ²⁺ 150 μm	Ni ²⁺ 250 μm
R ²	0.9412	0.5000
$K_p(\text{min}^{-1})$	4×10^{-5}	3×10^{-5}
D_F	-0.0266	-0.0264

The R² value of Ni²⁺ 250 μm suggests that the diffusivity model does not entirely support the adsorption of Ni²⁺ 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 figure 6 show that Ni²⁺ 250 μm is particle diffusion controlled while figure 7 show that Ni²⁺ 150 μm is film diffusion controlled since the plotted graph is non-linear. Since sorption of Ni²⁺ 250 μm is particle diffusion controlled (plot is linear), it could be affected by the following processes: (1) diffusion of the solute from the solution to the film surrounding the particle; (2) diffusion from the film to the particle surface (external diffusion); (3) diffusion from the surface to the internal sites (surface diffusion or pore diffusion); (4) uptake which can involve several mechanisms: physicochemical sorption, ion exchange, precipitation or complexation (Igwe *et al.*, 2005). 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 (juggle) 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 value confirms 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 metal ions for adsorption sites clearly affected the adsorption capacity (Igwe *et al.*, 2005).

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.

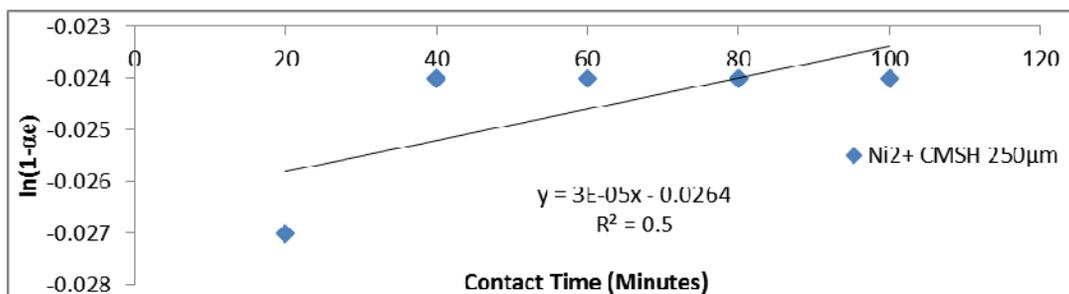


Fig 6: liquid film diffusivity model for cmsh 250 μm

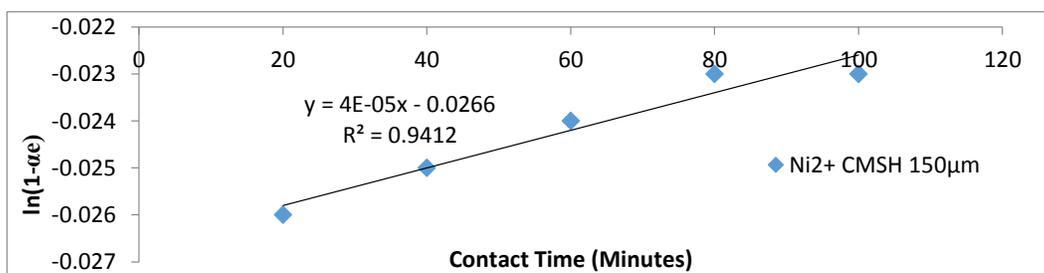


Fig 7: liquid film diffusivity model for cmsh 150 μm

3.3.2 Mass Transfer Model

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

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

Where,

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

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

T is the shaking time in minutes

D is the fitting diameter

K_o is a constant which is the mass transfer adsorption coefficient

A linearized form of the equation is written thus:

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

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

Table 5: mass transfer constants for cmsh 150 μm and 250 μm

Constants	Ni^{2+} 150 μm	Ni^{2+} 250 μm
R^2	0.0008	0.7370
D	21.982	22.594
K_o	1E-05	-0.0003

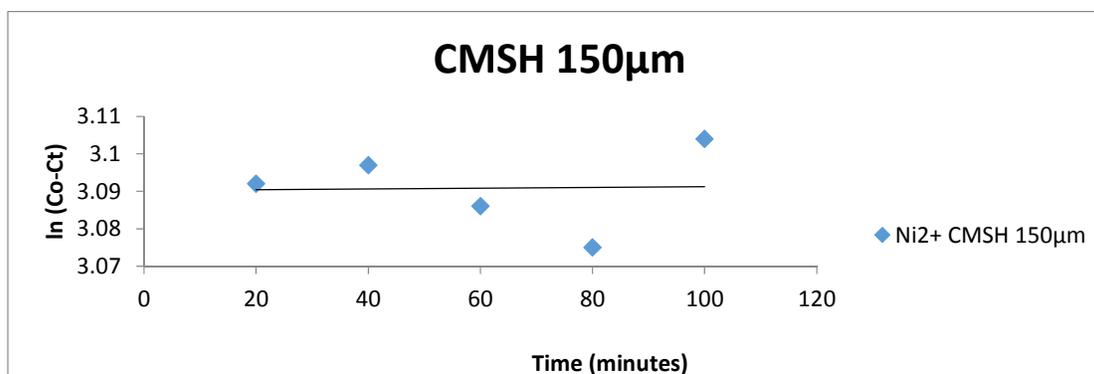


Fig 8: Mass Transfer Model of Metal Ions of Sample Pore Size CMSH 150 μm

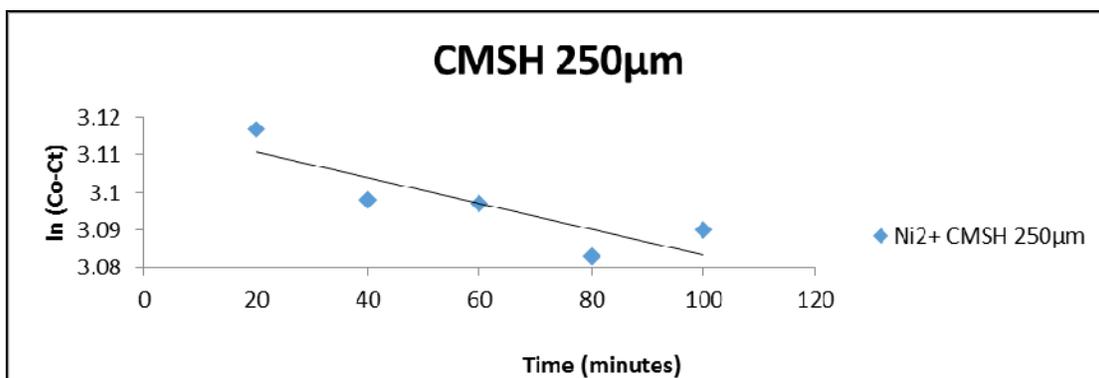


Fig 9: Mass Transfer Model of Metal Ions of Sample Pore Size CMSH 250 μm

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). These mechanisms (diffusion and mass transport by convection) were not supported suggesting that mass transfer model does not favour the sorption of Ni^{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 not very linear; suggesting that the sorption process is not diffusion and mass transport by convection controlled. The low R^2 values confirm this. Hence, diffusivity model parameters were then used as a film-diffusion controlled. Aikpokpodion Paul E. *et al.*, 2013 stated that the rate of diffusion of ions between soil solution and soil surfaces is generally low due to molecular collisions

that give rise to extremely strong hindrance to the movement of molecules.

3.3.3 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_{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 μm and 250 μm

Constants	Ni^{2+} 150 μm	Ni^{2+} 250 μm
R^2	0.0007	0.8264
$K_{id}(mgg^{-1}min^{-1(1/2)})$	2.8×10^{-3}	1.189×10^{-1}
C	37.983	36.973

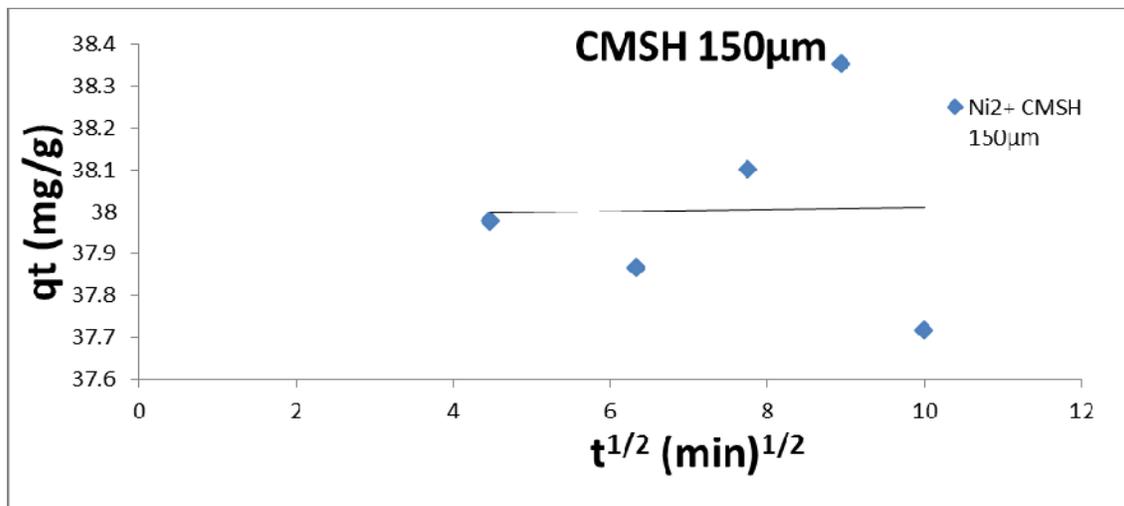


Fig 10: intra particle diffusivity model for cmsh 150 μm

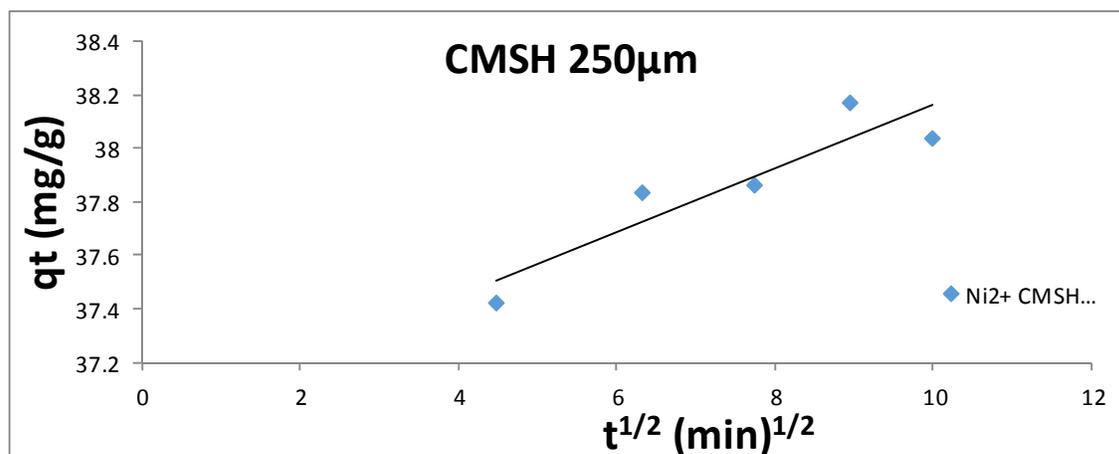


Fig 11: intra particle diffusivity model for cmsh 250 μm

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

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

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

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

3.3.4 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:

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

Linearising the equation, becomes

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

Where,

R is the percent of metal ion adsorbed

t is the contact time in minutes

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

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

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

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

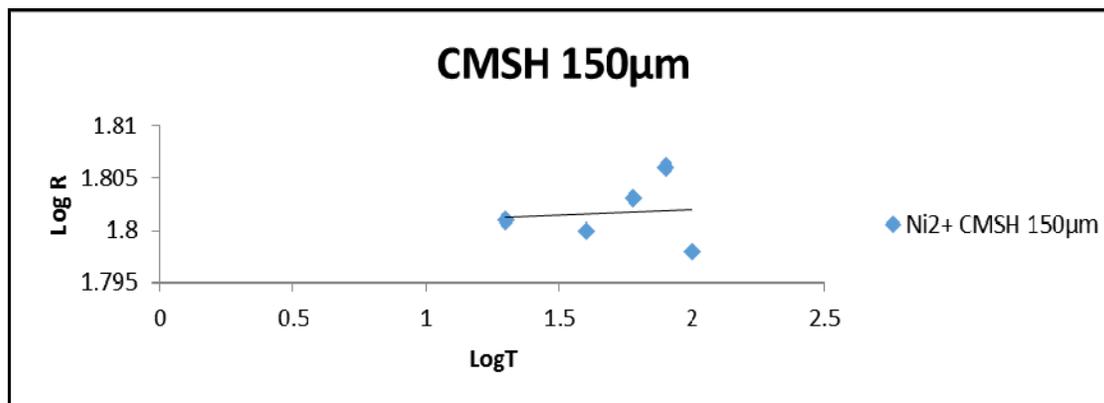


Fig 12: intra particle diffusion model for cmsh 150 μm

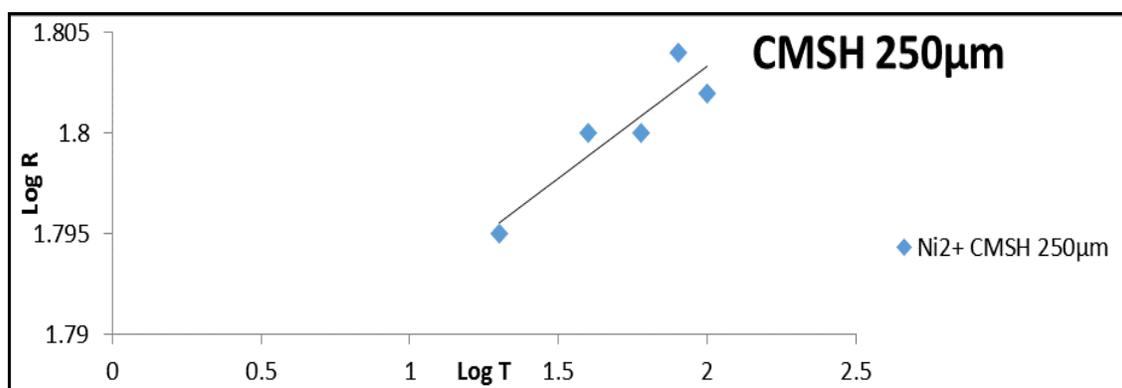


Fig 13: intra particle diffusion model for cmsh 250 μm

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 cmsh 150 μm and 250 μm

CONSTANTS	Ni ²⁺ 150 μm	Ni ²⁺ 250 μm
R^2	0.0090	0.3325
a	1×10^{-3}	2.35×10^{-2}
$K_{id}(\text{mgg}^{-1}\text{min}^{-1(1/2)})$	0.2552	0.2450

3.4 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. Micropores 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 Ni²⁺ from aqueous solution.

4. Conclusion

The conclusions based on experimental study were:

- Adsorbent preparation by carbonization and chemical modification of biosorbent using Mercapto acetic acid showed good affinity for the metal ion (Ni²⁺).
- The result obtained can be used for design purposes.
- These results can be used as a basis for the study of desorption and recovery of Nickel (II) from solution.

- Pore size analysis showed that 150 μm mesh had faster adsorption rate than 250 μm mesh, although both recorded high adsorption values.
- For liquid film diffusivity model, Ni²⁺ 150 μm favours film diffusion controlled adsorption while Ni²⁺ 250 μm favours particle diffusion controlled adsorption.

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