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Kinetics and Isotherm of Heavy Metal Adsorption on Activated Nigerian Coconut Shell and Corn Cob

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ABSTRACT
The performance of activated coconut shell and corn cob as adsorbent for adsorption of iron (II) ion (Fe^{2+}) and nickel (II) ion (Ni^{2+}) from aqueous solution was investigated. Effects of initial metal concentration, temperature, dosage, pH, particle size and contact time on the adsorption was also studied. Adsorption kinetics and isotherms used Adsorption process. Results of the amount of metals removed, increased with increase in adsorbent dosage and contact time, while increase in temperature, initial metal concentration and particle size decreased the adsorption percentage. Fe^{2+} adsorption reached equilibrium at about 120 minutes, while that of Ni^{2+} was attained at about 150 minutes in both adsorbents. The adsorbents were more effective in the removal of Fe^{2+} (up to 83% removal at optimal conditions) than Ni^{3+} (with up to 67% removal at optimal conditions), while coconut shell slightly outperformed activated corn cob. The second order kinetics fitted better than the first order and the intra-particle diffusion. Hence, the pseudo second order kinetics is most suitable for the adsorption process. Finally, the Langmuir, Freundlich and Temkin isotherms, all showed capability for interpretation of Fe^{2+} and Ni^{2+} adsorption onto activated coconut shell and corn cob. Therefore, it is recommended that activated coconut shell and corn cob be used for treatment of industrial effluent before disposal, to reduce environmental contamination.

KEYWORDS: Adsorption, Heavy Metals, Coconut, Corn- cob.

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1. INTRODUCTION
Environmental pollution all over the world is a concern, and it is persisted due the continuous activities of man, caused by advancement in technology. Industrialization growth causes major environmental concern due to the release of contaminants such as heavy metal ions according to (Ibrahim *et al*., 2016; Duru & Duru, 2017; Budi *et al*., 2018; Ujile & Okwakwam, 2018). Industries like electroplating and metal surfaces treatment, printed circuit board manufacturing, petroleum refining amongst others, released various types of pollutants from their effluents (Ibrahim *et al*., 2016; Ujile & Okwakwam, 2018). The degree of environmental impact depends on the properties, nature and quantity of pollutants (Al Zubaidy *et al*., 2015; Cirne *et al*., 2016; Fingas, 2018).

Hospitals, automobile repair workshops and paint industries also released inorganic and organic contaminants into the environment (Cirne *et al*., 2016; Abdullah & Choudhary, 2017; Dagde & Ndaka, 2019). The discharge of these wastes onto land and water environments before treatment could pollutes both surface and groundwater resources. The continuous pollution of the terrestrial environment without adequate management practice set-out to reduce the effect of pollution will definitely cause harm to the environment, humans, plants and animals exposed to area of pollution. According to Ujile and

Owhor (2018), appropriate waste disposal strategies in most developing countries are not in practice, which has resulted to environmental challenges. Rivers State, as host to many industries is faced with several environmental pollution. Besides the industries, there are also automobile mechanic workshops and hospitals. Because of the inherent diseases such as hepatitis, diarrhea, cholera and cancer can occur by consuming contaminated water, it is necessary that proper screening and remedial process be applied on water system to ascertain its suitability for consumption.

Several technologies for the removal of toxic substances like heavy metals, total solids, organics and biological contaminants from wastewater are available (Moussavi & Barikbin, 2010), but some of these technologies are capital intensive and are only efficient to some extent (Ideriah *et al*., 2012). One economic and efficient method for the removal of metallic and organic contaminants from wastewater is the adsorption technique (Ndamitso *et al*., 2016; Abdullah and Choudhary, 2017; Budi *et al*., 2018; Dagde and Ndaka, 2019). Adsorption technique is simple to operate, and it is environmentally friendly, cost-effective. Adsorption technique is used for the removal of heavy metals from aqueous solution (Jimoh *et al*., 2012; Ademiluyi and Ujile, 2013; Ujile and Joel, 2013; Ujile and Okwakwam, 2018). Adsorption process can be achieved through the use of locally available agricultural based materials, such as palm fruit fibre, rice husk, garlic, ginger, bamboo, onions and Soursop (Ideriah *et al*., 2012; Ademiluyi and Ujile, 2013; Ndamitso *et al*., 2016; Swarnalakshmi *et al*., 2018; Dagde and Ndaka, 2019). Most agricultural wastes such as coconut shell contain carbon, hydrogen, oxygen and ash (Budi *et al*., 2018). The use of agricultural wastes as adsorbent can be modified by physical or chemical activation. Studies have shown that carbon content in most agricultural wastes increased up to 76.32 % when pyrolized into charcoal with high porosity and large surface area, which are important for adsorption process (Mozammel *et al*., 2002; Budi *et al*., 2018). Activation of waste also consumes less electrical energy, reduces toxicity and global warming (Arena *et al*., 2016; Sulyman *et al*., 2017).

Analysis carried out on water samples collected within the premises of a hospital, automobile workshop and paint manufacturing industry, at various locations in Port Harcourt city, showed that the water samples were highly contaminated by heavy metals. Though, many adsorbents have been used to treat waste water, but comparison of the capacity of activated coconut shell and corn cob in adsorption of heavy metals are scarce. Therefore, this study investigated the adsorption capacity of activated coconut shell and corn cob as adsorbents for the removal of iron (II) and nickel (II) ions from aqueous solution.

2. MATERIALS AND METHODS

2.1 Sample Collection

Coconut shell and corn cob were collected from Isiokpo in Ikwerre Local Government Area of Rivers State.

2.2 Carbonisation of Samples

The adsorbents were prepared according to the method described in Bisht *et al*. (2020). First, the materials were sun-dried for 2 days, and then, ½washed with deionised water to remove soluble impurities. After deionization, the materials were further dried in the oven at 70 °C for (½) half hour. The dried samples were weighed on analytical weighing balance to determine the bulk weight before carbonization. After weighing, the prepared coconut shell and corn cob were pyrolized at temperature range of 500–800ºC. The carbonaceous material obtained was pulverized to obtain fine particle sizes.

2.3 Activation of Carbonaceous Materials

2000 cm^3 (2 litre) of water was measured via graduated cylinder into a vessel. Also, 87 cm^3 of

1.0 M HCl (hydrochloric acid) was measured and poured into the vessel with water. 2000g weight of the sieved carbonaceous material was added into the mixture and stirred vigorously for activation. The mixture was allowed to settle for 24 hours, and washed using distilled water to remove the acid content. The level of acidity was determined using litmus paper test. After washing, the material was air dried for about 72 hours. The activation process helps to increase the surface area and functional groups, as this would enhance the adsorption capacity of the adsorbents (Hui & Zaini, 2015). The activated adsorbents were sieved to different particle sizes.

2.4 Adsorption Experiment

The heavy metal concentration was determined using the Atomic Adsorption Spectrophotometer (AAS) after each experimental run.

2.4.1 Effect of Initial Concentration

10, 20, 30, 40 and 50 mg/L initial concentrations of iron (II) and Ni (II) ions were prepared from iron (II) nitrate ($Fe(NO_3)_2$) nickel nitrate ($Ni(NO_3)_2.6H_2O$), and added into beaker containing 250ml of distilled water. Other parameters were kept constant at 1.0g adsorbent dosage, 6.5 solution pH, and 600µm particle size while the temperature was maintained at room temperature. In each initial concentration, the process was allowed to stir for 120 minutes before being decanted through the filter paper.

2.4.2 Effect of Temperature

The effect of temperature was studied at ambient temperature, 40, 50, 60 and 70ºC, while other parameters were kept constant.

2.4.3 Effect of Solution pH

The effect of pH was studied at pH of 4.5, 5.5, 6.5, 8.0 and 9.0. After each experimental run, the sample was taken for analysis. The pH of the solution was adjusted by adding either hydrochloric acid or sodium hydroxide.

2.4.4 Effect of Dosage

Effect of adsorbent dosage was studied at different weighs of 0.5, 0.75, 1.0, 1.25 and 1.5g.
l

2.4.5 Particle Size

The effect of particle size was studied at 300µm, 600µm, 1.8mm, 2.18mm and 2.23mm, while other parameters were kept constant.

2.4.6 Contact Time

Effect of contact time was studied at 30, 60, 90, 120 and 180 minutes, while other parameters were kept constant.

2.5 Calculation of Adsorbed Metals

The percentage of Fe^{2+} and Ni^{2+} adsorbed onto the adsorbents was calculated using the formula.

$$\text{Adsorbed metal}(\%) = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

The adsorption capacity at equilibrium was calculated using formula.

$$Q_e = (C_i - C_e)\frac{V}{w} \quad (2)$$

The adsorption capacity with time was calculated using formula:

$$Q_t = (C_i - C_t)\frac{V}{w} \quad (3)$$

where:
Q_e = Adsorption capacity at equilibrium (mg/g)
Q_t = Adsorption capacity at time, t (mg/g)
C_f = Final concentration of metal ion in the liquid mixture (mg/l)
C_i = Initial concentration of metal ion in the liquid mixture (mg/l)
C_e = Concentration of metal ion in the liquid mixture at equilibrium (mg/l)
V = Volume of liquid mixture (l)
w = Weight of adsorbent (g)

2.6 Adsorption Kinetic Study

2.6.1 Pseudo First Order Kinetics

The pseudo first order model expressed by Ho (2004) as:

$$\log(Q_e - Q_t) = \log Q_e - k_1 t \quad (4)$$

Where:

k_1 = Pseudo first order adsorption rate constant (min^{-1})

Q_e = Concentration of heavy metal adsorbed by the adsorbent at equilibrium (mg/g)

Q_t = Concentration of heavy metal adsorbed by the adsorbent with time (mg/g)

t = Measured time of adsorption (min)

The plot of $\log(Q_e - Q_t)$ versus t gives slope equivalent to k_1 and intercept equivalent to $\log Q_e$.

2.6.2 Pseudo Second Order Kinetics

The pseudo second order kinetics is expressed as (Ho, 2004):

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{Q_e^2 k_2} \quad (5)$$

The plot of $\frac{t}{Q_t}$ against t gives slope as $\frac{1}{Q_e}$ and intercept as $\frac{1}{Q_e^2 k_2}$.

Where:

k_2 = Pseudo second order adsorption rate constant (g/gm.min)

2.6.3 Intra-Particle Diffusion Model

The intra-particle diffusion kinetics developed by Weber and Morris in 1963 had been applied for adsorption contaminants. This was expressed according to Pasavant *et al*. (2006) as:

$$Q_t = K_d \sqrt{t} \quad (6)$$

Where:

Q_t = The amount adsorbed at time t (mg/g)

K_d = Weber and Morris intra-particle diffusion rate constant (mg/g.min$^{0.5}$)

t = Time of adsorption (min)

The plot of Q_t versus $t^{1/2}$ gives a slope equivalent to K_d, and the linearity of the plot is an indication that the adsorption follows intra-particle diffusion (Pasavant *et al*., 2006).

2.7 Adsorption Isotherm

2.7.1 Langmuir Isotherm Model

The Langmuir isotherm model has been used by many researchers as expressed in the work of Ademiluyi and Ujile (2013).

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

Re-arranging equation (7) gives

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (8)$$

A plot of $\frac{C_e}{Q_e}$ versus C_e gives a straight line graph with slope equivalent to $\frac{1}{Q_m}$ and the intercept as $\frac{1}{K_L Q_m}$.

Where:

Q_m = Maximum adsorption capacity (mg/g)

K_L = Energy of adsorption (L/mg)

To further investigate the reliability of the adsorbent, Langmuir isotherm parameters was used to evaluate the separation factor or adsorption intensity R_L, which is expressed as follow (Ademiluyi and Ujile, 2013).

$$R_L = \frac{1}{1 + K_L C_i} \quad (9)$$

The separation factor R_L, is one of the important indicators in adsorption process. Thus, when $0<R_L<1$, it indicates that adsorption is favorable; when $R_L>1$, it indicates adsorption is not favorable; when $R_L=1$, it indicates adsorption is linear; and when $R_L=0$, it indicates adsorption is irreversible (Ademiluyi and Ujile, 2013 and Shama *et al*. 2016).

2.7.2 Freundlich Isotherm

The Freundlich isotherm is expressed as (Opeolu *et al*., 2009).

$$Q_e = K_f C_e^{1/n} \qquad (10)$$

To obtain the constants, the logarithm of both sides of equation (10) was taken to give

$$\ln Q_e = \ln K_f + \frac{1}{n}\log C_e \qquad (11)$$

A plot of $\ln Q_e$ versus $\ln C_e$ gives the slope of the graph as $\frac{1}{n}$ and the intercept as $\log K_f$.

Where:
K_f = Freundlich constant
n = Heterogeneity of the adsorption energy across the adsorbent surface

2.7.3 Temkin Isotherm Model

Temkin isotherm model is expressed according to Sharma *et al*. (2016) as:

$$Q_e = \frac{RT}{b}\ln(AC_e) \qquad (12)$$

Equation (12) can be expanded as follows:

$$Q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e \qquad (13)$$

Further simplification yields:

$$Q_e = B\ln A + B\ln C_e \qquad (14)$$

A and B are obtained from the plot of Q_e against $\ln C_e$.

Where:
R = Gas constant (J/mol.K)
T = Adsorption temperature (K)
b = Constant relating to adsorption energy across the adsorbent surface (J/mol)
A = Temkin constant relating to adsorption capacity (L/mg)

3. RESULTS AND DISCUSSION

3.1 Effect of Adsorption Parameters on Heavy Metal Removal

3.1.1 Effect of Initial Concentration

The effect of initial concentration of iron (II) ion (Fe^{2+}) and nickel (II) ion (Ni^{2+}) on the adsorption capacity of coconut shell and corn cob particles was studied at constant pH of 6.5, contact time of 120 min, adsorbent dosage of 1.0 g, particle size of 600 µm and at ambient temperature of 27ºC (room temperature), while the initial concentration of the respective heavy metals was varied from 10mg/L to 50mg/L.

The profiles of Fe^{2+} and Ni^{2+} removed from the polluted water by activated coconut shell and corn cob particles, as influenced by the concentration of the heavy metals in the solution, are shown in Figure 1. The percentage of the metals removed from the solution increases rapidly and then, decreases gradually as the initial concentration of the metals was increased from 10 to 50mg/L.

Thus, from 10 – 50mg/L initial concentration, the percentage of the metal removed by coconut shell decreased from 83.54 – 68.10% for iron (II) ion (Fe^{2+}) and 69.85 –55.98% for nickel (II) ion (Ni^{2+}), while with corn cob, the percentage decreased from 80.65 – 65.74% for Fe^{2+} and 67.43 –54.05% for Ni^{2+}. The percentage of the heavy metals adsorbed from the aqueous solution differs. Thus, the percentage of Fe^{2+} adsorbed onto both adsorbents was more than Ni^{2+}. This implied that Fe^{2+} has stronger affinity to the activated coconut shell and corn cob adsorbent than Ni^{2+}. Okafor *et al*. (2012) also observed higher removal of lead ion by coconut shell than cadmium ion (Pb^{2+}>Cd^{2+}) mixed in same solution.

Several studies on adsorption of heavy metal adsorbed onto coconut shell, corn cob or other bio-adsorbents, as initial metal concentration increased have also shown that increase in initial concentration of heavy metal in an aqueous solution resulted in lower percentage removal

(Sartape *et al*., 2012; Ademiluyi & Ujile, 2013; Song eit *al*., 2014; Bamukaye & Wanasolo, 2017; De Angelis *et al*., 2017; Mashangwa *et al*., 2017). The reduction in percentage removal of heavy metal adsorbed when the initial concentration of contaminants was increased, at constant adsorbent dosage, is attributed to increase in the amount of metals in the solution, which occupied all the available vacant sites on the adsorbent surface, thereby, making the adsorbent saturated such that only the attached molecules were removed (Dawodu *et al*., 2012; Bamukaye and Wanasolo, 2017). In contrary, Okafor *et al*. (2012) reported increase in Cu^{2+}, Pb^{2+}, Cd^{2+} and As^{3+} adsorbed onto coconut shell when initial metals concentration was increased from 0.5 to 5mg/L. This was due to the small initial metal concentration of the metals in the solution, which is small compared to the available vacant sites on the adsorbents (Kumar & Shrivastava, 2015; Sharma *et al*., 2016).

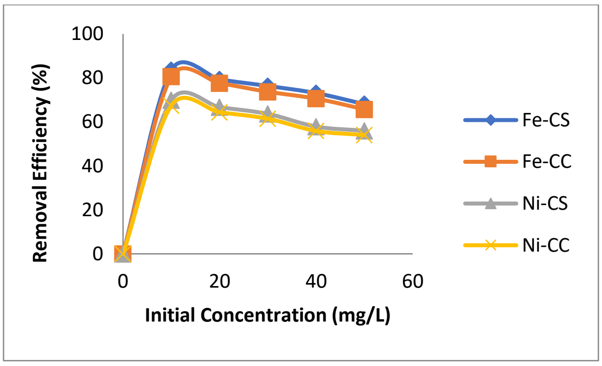

Figure 1: Metal removed versus initial concentration

3.1.2 Effect of Temperature

Effect of temperature was studied at 27 ºC (room temperature), 40, 50, 60 and 70 ºC, while other parameters were kept constant at 10mg/L initial concentrations, 6.5 pH, 1.0g dosage, 600µm particle size and 120 min contact time.

The effect of temperature on Fe^{2+} and Ni^{2+} adsorption onto coconut shell and corn cob particles is shown in Figure 2. From the experimental observation, the percentage of Fe^{2+} and Ni^{2+} adsorbed decreased with temperature increase. From 27 – 70 ºC, the percentage of the metal removed by coconut shell decreased from 83.54 – 75.18% for Fe^{2+} and 69.85 –61.22% for Ni^{2+}, while with corn cob, the percentage decreased from 80.65 – 74.30% for Fe^{2+} and 67.43 –60.79% for Ni^{2+}. Again, the percentage of Fe^{2+} adsorbed onto both adsorbents was more than Ni^{2+}.

The reduced percentage of Fe^{2+} and Ni^{2+} adsorbed as temperature increases can be attributed to rise in the average kinetic energy, which disrupted already adsorbed molecules onto the adsorbent and those in the solution. Bhaumik *et al*. (2012) attributed the decreasing percentage removal of contaminants in solution to decrease in thickness of boundary layer caused by the escaping molecules from the adsorbent. Similar results were also observed by other authors, as regard the effect of temperature on adsorption (Ciobanu *et al*., 2016; Abd Elhafez *et al*., 2017). These studies also observed that temperature increase leads to exothermic process in adsorption.

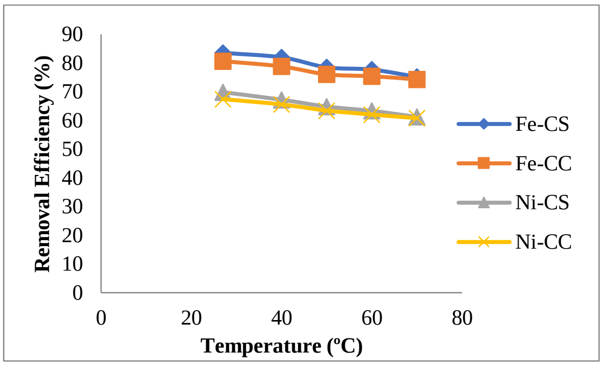

Figure 2: Metal removed versus temperature

3.1.3 Effect of pH

Effect of pH was studied at 4.5, 5.5, 6.5, 8 and 9, while other parameters were kept constant at 10mg/L initial concentrations, 27 ºC temperature, 1.0g dosage, 600µm particle size and 120 min contact time.

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The effect of pH on Fe^{2+} and Ni^{2+} adsorption onto coconut shell and corn cob particles is shown in Figure 3. The percentage of Fe^{2+} and Ni^{2+} adsorbed increases initially as pH increased from 4.5 to 6.5 (i.e. from 67.87 to 83.54% for Fe^{2+} and from 60.12 to 69.85 for Ni^{2+} onto coconut shell and from 67.65 to 80.65% for Fe^{2+} and from 55.34 to 67.43 for Ni^{2+} onto coconut shell) and then, decreases gradually to 81.20%, 76.86%, 67.94% and 64.96% at pH of 9 for Fe^{2+} on coconut shell, Fe^{2+} on corn cob, Ni^{2+} on coconut shell, and Ni^{2+} on corn cob, respectively. The results obtained for effect of pH agreed with the work of adsorption of Bamukyaye and Wanasolo (2017).

Studies have shown that, in acidic solution, the functional groups present are dominated by positively charged protons on adsorbent surface, and this reduces the adsorption capacity due to repulsion of like charges (Rao and Prabhakar, 2011; Khalili *et al*., 2012).

Mashangwa *et al*. (2017) showed that increase in pH also increased the availability of hydrozonium ion (H_3O^+) competing with the metals ions on the adsorption sites of the adsorbents.

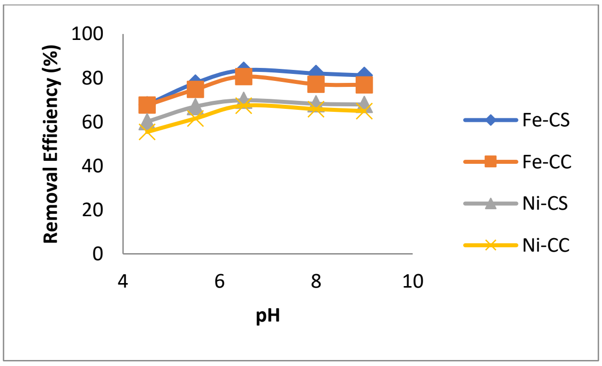

Figure 3: Metal removed versus pH

3.1.4 Effect of Adsorbent Dosage

Effect of adsorbent dosage was studied at 0.5, 0.75, 1.0, 1.25 and 1.5g. Other parameters were kept constant at 10mg/L initial concentration, 27°C temperature, 6.5 pH, 600µm particle size and 120 min contact time.

The effect of dosage on Fe^{2+} and Ni^{2+} removal by coconut shell and corn cob particles is shown in Figure 4. The results showed that the percentage of Fe^{2+} and Ni^{2+} adsorbed increased with increase in adsorbent dosage. From 0.5 – 1.5g, the percentage of Fe^{2+} and Ni^{2+} removed by coconut shell increased from 72.75 – 85.09% and 60.82 – 71.14%, respectively. Similarly, the percentage of Fe^{2+} and Ni^{2+} removed by corn cob increased from 70.23 – 82.14% and 58.72 – 68.68%, respectively.

These results agreed with other studies on the effect of dosage on heavy metal adsorption (Bamukaye and Wanasolo, 2017; Mashangwa *et al*., 2017; Badrealam *et al*. 2018).

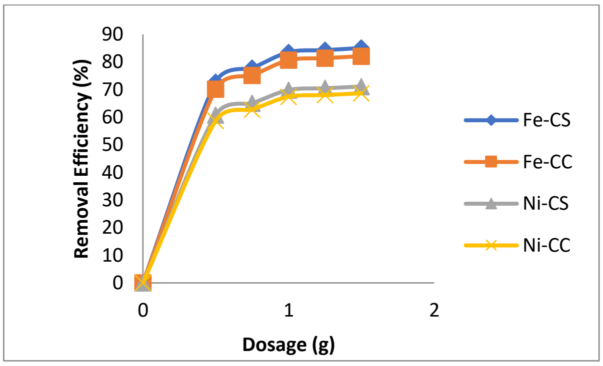

Figure 4: Metal removed versus dosage

3.1.5 Effect of Particle Size

Effect of particle size was studied at 300µm, 600µm, 1.18mm, 2.18mm and 2.23mm. Other parameters were kept constant at 10mg/L initial concentration, 27 °C temperature, 6.5 pH, 1.0g dosage, and 120 min.

The effect of particle size on Fe^{2+} and Ni^{2+} removal by coconut shell and corn cob particles is shown in Figure 5. The results showed that the percentage of Fe^{2+} and Ni^{2+} adsorbed decreased with increase in particle size. Thus, from 0.0003 (300µm) – 2.23mm, the percentage of Fe^{2+} and Ni^{2+} removed by coconut shell decreased from 85.20 – 75.44% and 71.23 –63.08%, respectively, while the percentage of Fe^{2+} and Ni^{2+} removed by corn cob decreased from 82.25 – 72.83% and 68.77 – 60.89%, respectively.

The increase
in removal can be attributed to increased surface area at smaller particle sizes, which equally increased the binding site (Emenike *et al*., 2016; Abd elhafez *et al*., 2017)

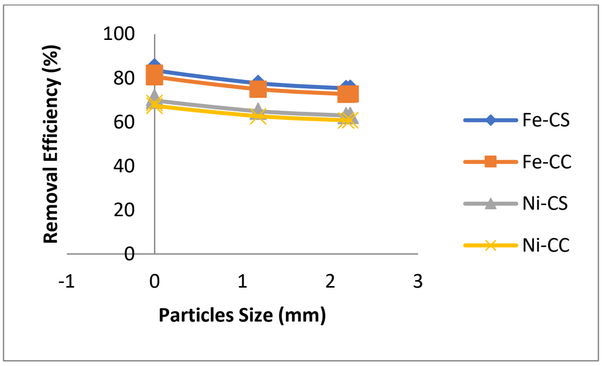

Figure 5: Metal removed versus particle size

3.1.6 Effect of Contact Time

Effect of contact time was studied at contact time of 30, 60, 90, 120 and 180 minutes. Other parameters were kept constant at 10mg/L initial concentration, 27 ºC temperature, 6.5 pH, 1.0g dosage and 600µm particle size.

The effect of contact time on Fe^{2+} and Ni^{2+} adsorption onto coconut shell and corn cob particles is shown in Figure 6. The percentage of Fe^{2+} and Ni^{2+} adsorbed increased with increase in contact time. Thus, from 30 – 180 min, the percentage of Fe^{2+} and Ni^{2+} removed by coconut shell increased from 58.48 – 86.05% and 48.89 – 71.94%, respectively, while onto corn con, the percentage of Fe^{2+} and Ni^{2+} removed increased from 54.86 – 83.80% and 45.86 – 70.06%, respectively.

It was observed that from 120 minutes, the amount of Fe^{2+} adsorbed onto coconut shell and corn cob only increased slightly, while this was noticed at about 150 minutes for Ni^{2+}. This is an indication that equilibrium adsorption may not be attained at the same time in both metals.

This is in agreement with some other studies on effect of contact time on heavy metal adsorption (Tabatabaee *et al*., 2016; Mashangwa *et al*., 2017; Badrealam *et al*. 2018).

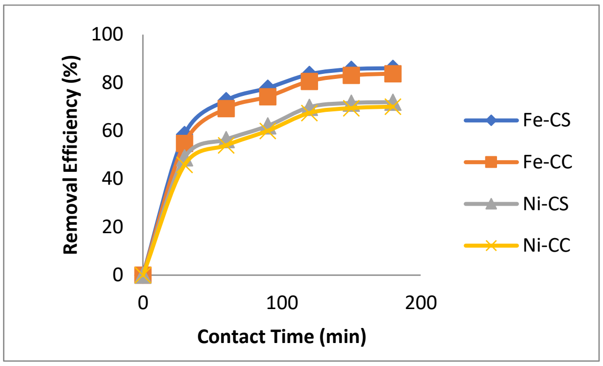

Figure 6: Metal removed versus contact time

3.2 Kinetics of Heavy Metal Adsorption

The kinetics of Fe^{2+} and Ni^{2+} adsorption onto the adsorbents was studied to determine the best fit kinetic model that describes the adsorption process. Figure 7 shows the plots of the first order kinetics, while Figures 8 and 9 are the plots of the second order kinetics and intra-particle diffusion models for Fe^{2+} and Ni^{2+} adsorbed onto activated coconut shell and corn cob. From the linear equations on Figure 7, the first order rate constant, k_1 was obtained. Also, from Figure 8, the second order rate constant, k_2 was obtained, while the constants relating to the intra-particle diffusion were obtained through Figure 9. The kinetic constants and adsorption capacity at equilibrium obtained from the model are shown in Table 1.

However, the intra-particle diffusion rate constant, K_d, for adsorption of Fe^{2+} onto coconut shell and corn cob was obtained as 0.0519 mg/g.min$^{0.5}$ and 0.0545 mg/g.min$^{0.5}$ respectively, while for adsorption of Ni^{2+} onto coconut shell and corn cob, it was obtained as 0.047mg/g.min$^{0.5}$ and 0.0488mg/g.min$^{0.5}$ respectively. The equilibrium adsorption capacity, Q_e, obtained from the second order model was closer to values obtained from the experiment than that calculated from the first order model. This showed that the second other described the experimental data better. This agreed with reported studies on comparison of adsorption process by the second order pseudo kinetics (Sharma *et al*., 2016; Azizi *et al*., 2017; Dagde and Daka, 2019; Chie-Amadi *et al*., 2020). From the intra-particle diffusion plots, the linear lines did not pass through the origin, and failure of the linear plots to pass through the origin means the adsorption process was not controlled by intra-particle diffusion (Ademiluyi & Ujile, 2013).

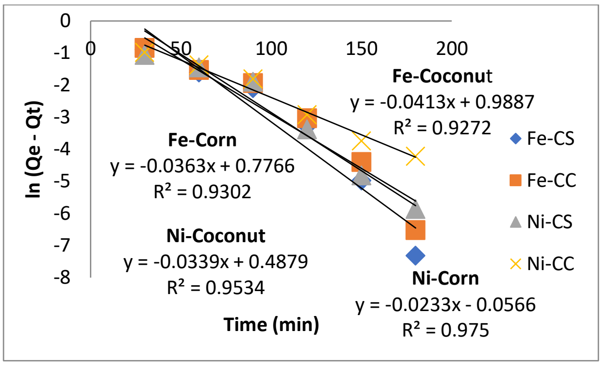

Figure 7: Plot for 1st order kinetic data analysis

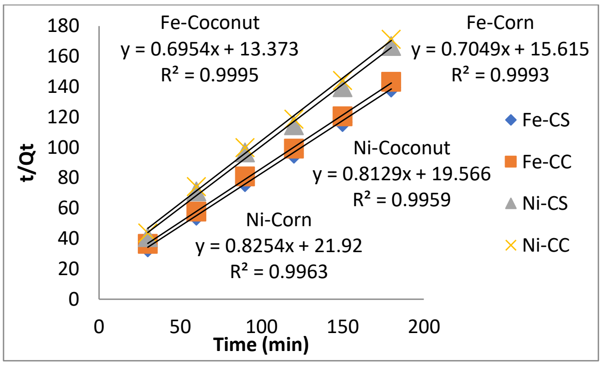

Figure 8: Plot for 2nd order kinetic data analysis

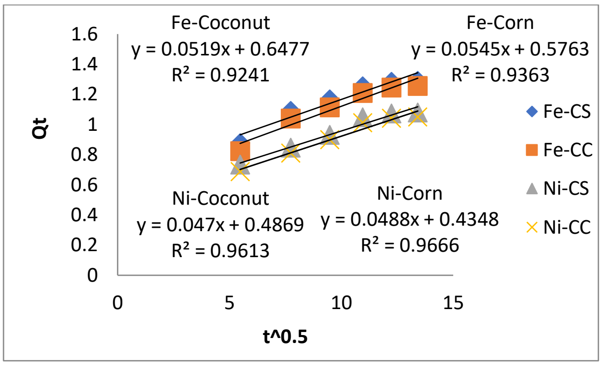

Figure 9: Plot for Intra-particle diffusion data analysis

Table 1: Summary of Kinetic Parameters

	1st Order					
	k_1 (min^{-1})		**Qe (mg/g)**		**R^2**	
Metal	**Coconut**	**Corn**	**Coconut**	**Corn**	**Coconut**	**Corn**
Fe	0.0413	0.0363	2.6877	2.17407	0.9272	0.9302
Ni	0.0339	0.0233	1.6289	0.94497	0.9534	0.975
	2nd Order					
	k_2 (g/mg.min)		Qe (mg/g)		R^2	
Fe	0.0362	0.0318	1.4380	1.4186	0.9995	0.9993
Ni	0.0302	0.0348	1.2302	1.2115	0.9959	0.9963

3.3 Adsorption Isotherms

3.3.1 Langmuir Isotherm

Figure 10 shows plots for evaluation of Langmuir isotherm parameters for adsorption of Fe^{2+} and Ni^{2+} onto coconut shell and corn cob. From the plots, the maximum adsorption capacity, Q_m for Fe^{2+} adsorption onto coconut shell and corn cob was obtained as 8.9286mg/g and 7.4460mg/g, respectively, while the Langmuir constant was obtained as 0.1129L/g and 0.1249L/g, respectively. Also, the maximum adsorption capacity, Q_m for Ni^{2+} adsorption onto coconut shell and corn cob was evaluated as 7.1327mg/g and 7.3153mg/g, respectively, while the Langmuir constant was obtained as 0.0648L/g and 0.0574L/g, respectively.

Based on the Langmuir isotherm, Fe^{2+} adsorption onto coconut shell has the highest maximum adsorption capacity. The performance of Langmuir isotherm in this study also agreed with some previous studies on heavy adsorption onto coconut and corn cob (Song *et al*., 2014; Idah *et al*., 2016; Muthusamy & Murugan, 2016; Singh and Waziri, 2019).

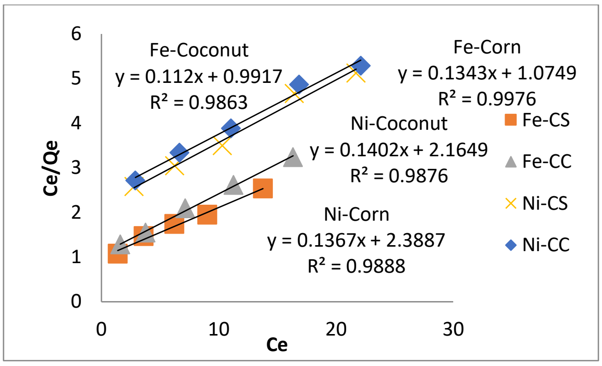

Figure 10: Langmuir adsorption isotherm

Table 2: Langmuir isotherm parameters

Metal	Qm (mg/g	KL (L/g)	R^2
Fe-Coconut	8.9286	0.1129	0.9863
Fe-Corn	7.4460	0.1249	0.9976
Ni-Coconut	7.1327	0.0648	0.9876
Ni-Corn	7.3153	0.0574	0.9888

Further analysis on the adsorption process, utilising the Langmuir dimensionless parameter, called separation factor, R_L, revealed that the adsorption of Fe^{2+} and Ni^{2+} onto coconut shell and corn cob is favourable. The profiles are shown in Figure 11. R_L values ranged between 0.15 – 0.64. The range of separation factor obtained in this study is within reported values for bio-sorption (Sharma *et al*., 2016; De-Angelis *et al*., 2017).

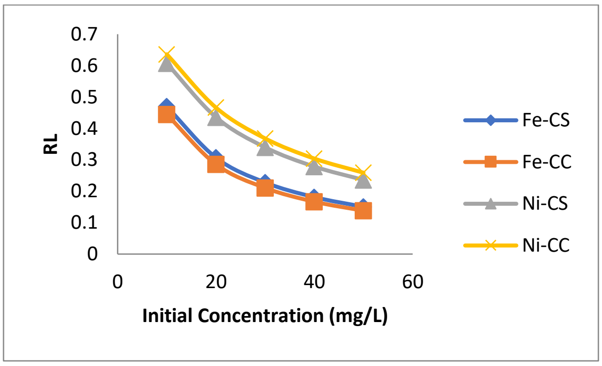

Figure 11: Plot for separation factor

3.3.2 Freundlich Isotherm

Figure 12 shows plots for evaluation of Freundlich isotherm parameters for adsorption of Fe^{2+} and Ni^{2+}. From the plots, the Freundlich adsorption isotherm parameters: n and K_f were obtained as shown in Table 3.

Based on R^2 values, the Freundlich isotherm performed excellently as the Langmuir isotherm for adsorption of Fe^{2+} and Ni^{2+} onto coconut shell and corn cob. Song *et al*. (2014) also observed high performance of Freundlich isotherm in adsorption of Pb^{2+} onto coconut shell, but in other studies, the performance of the Freundlich isotherm was rated below the Langmuir isotherm (Idah *et al*., 2016; Muthusamy & Murugan, 2016; Singh and Waziri, 2019).

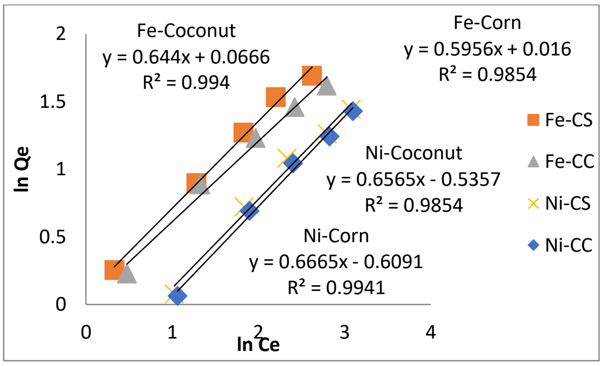

Figure 12: Freundlich adsorption isotherm

Table 3: Freundlich isotherm parameters

Metal	*n*	K_f (mg/g)	R^2
Fe-Coconut	1.5528	1.0689	0.9940
Fe-Corn	1.6790	1.0161	0.9854
Ni-Coconut	1.5232	1.7086	0.9854
Ni-Corn	1.5004	1.8388	0.9941

3.3.4 Temkin Isotherm

Figure 13 shows plots for evaluation of Temkin isotherm parameters for adsorption of Fe^{2+} and Ni^{2+}. The evaluated Temkin isotherm parameters are shown in Table 4.

Based on R^2 values, Temkin isotherm also fitted the experimental results, and compared with the Langmuir isotherm. Muthusamy and Murugan (2016) showed that Temkin isotherm fitted well with experimental data than the Langmuir and

Freundlich
isotherms in adsorption of the metals onto corn cob, but in Song *et al*. (2014), the reverse was the case.

Generally, this study showed that either of the adsorption isotherms can be used to study the adsorption heavy metals in polluted water.

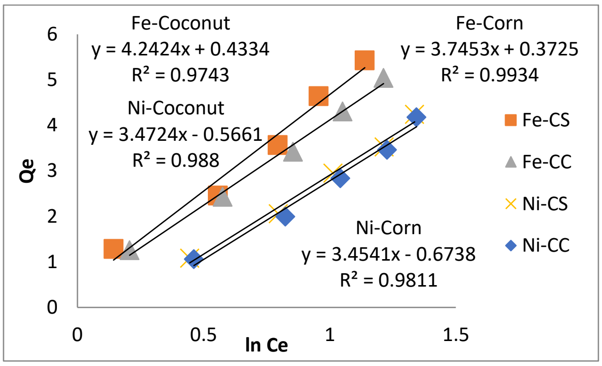

Figure 13: Temkin adsorption isotherm

Table 4: Temkin isotherm parameters

Metal	b (J/mol)	A (L/mg)	R^2
Fe-Coconut	587.922	1.0007	0.9743
Fe-Corn	665.955	1.0006	0.9934
Ni-Coconut	718.293	1.0008	0.9880
Ni-Corn	722.098	1.0009	0.9811

4. CONCLUSION

The adsorption of Fe^{2+} and Ni^{2+} onto coconut shell and corn cob from aqueous solution is affected by initial metal concentration, temperature, pH of the solution, adsorbent dosage, particles size and contact time. While increase in adsorbent dosage and contact time favoured the adsorption process, excessive increase in initial metal concentration, pH, temperature and particle size could impair of the performance of adsorbent. Therefore, in chosen the condition for adsorption, care must be taken to obtain an optimum adsorption capacity.

The study also showed that the kinetics of Fe^{2+} and Ni^{2+} adsorption onto coconut shell and corn cob can be best described as external diffusion and chemisorption, while adsorption process can be studied by Langmuir, Freundlich or Temkin isotherm. Finally, the high adsorption capacity recorded in the study indicates that activated coconut shell and corn cob can be used for the treatment of industrial wastewater.

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