Dynamic Adsorption Studies for the Removal of Cd (II) and Ni (II) from Aqueous Solutions using Mahogany Leaves

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ABSTRACT

A dynamic adsorption study was carried out using mahogany leaves (ML) powder as an adsorbent for the removal of Cd (II) and Ni (II) from their aqueous solutions. The effects of contact time, adsorbent dose (5, 10 and 15 g), initial concentration (10, 15 and 20 mg/L), particle size (212, 150 and 106 µm) and pH of zero charge (pH_{pzc}) on the adsorption of Cd (II) and Ni (II) ions onto mahogany leaves powder at pH of 4.5 were investigated. The results showed that, an increase in contact time and adsorbent dose increase the percentage removal of metals. The adsorption was found to be more effective at higher concentrations of metals and with smaller adsorbent particle size. The physicochemical characteristics of the adsorbent such as attrition loss, moisture content, bulk density, pore (void) volume, iodine number/surface area, SEM and FTIR of the stationary phase were investigated. Modelling of dynamics of the fixed-bed adsorption process was studied, and the application of different models to describe the breakthrough curves showed that, Yoon–Nelson is the best fit model with values of correlation coefficient R^2 of 0.9048 and 0.8557 for cadmium and nickel respectively gave better results for the operating conditions. Recommendation was made such that, mahogany leaves should be studied for the remediation of other heavy metals, such as lead, chromium, mercury, zinc and uranium among others.

INTRODUCTION

Removal of heavy metals from water and wastewater is important in order to protect public health and the environment. Methods of removing these metals include chemical precipitation, membrane filtration, ion exchange, reverse osmosis, liquid extraction or electro-dialysis (Kumar *et al*., 2012 and Achanai *et al*., 2012). However, these processes have considerable disadvantages including incomplete metal removal especially at low concentrations, requirement of expensive equipment and monitoring systems, large amount of reagents or energy requirements and generation of toxic sludge or other waste products that require disposal (Kumar *et al*., 2012). Therefore, the search for new technologies for the removal of heavy metals from aqueous media has been directed towards adsorption as a cost-effective and eco-friendly technique used in wastewater treatment over the last few decades (Egila *et al*., 2011).

Dynamic Adsorption

This is a technique that uses a solid stationary phase, (the adsorbent) packed in a glass column, and a solvent, (the mobile phase) that moves slowly through the packed column under the influence of gravity and pressure. The mobile phase is called the eluent, and the liquid that flows out of the end of the column is called the eluate (Bahl, Bahl and Tuli, 2012). El-Kamash (2008), used zeolite A as an adsorbent to remove Cs^+ and Sr^{2+} ions from aqueous solutions using similar method. Baral *et al*., (2009), removed Cr (VI) by thermally activated weed *Salvinia cucullata* in a fixed-bed column. Agrawal and Bajpai (2011), studied dynamic column adsorption studies of toxic Cr(VI) ions on to iron oxide loaded with gelatin nanoparticles. Ahmad and Hameed (2010), conducted a research on fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste.

MATERIALS AND METHODS

Reagents used were Cadmium (II) nitrate tetrahydrate, $[Cd(NO_3)_2.4H_2O]$, Nickel (II) nitrate hexahydrate, $[Ni(NO_3)_2, 6H_2O]$, Nitric acid, HNO_3, Ammonium hydroxide, NH_4OH, Distilled water and Mahogany leaves. All the necessary chemicals used in the study were of analytical grade, obtained by May & Baker Ltd., Dagenham, England as

provided by the Department of Pure and Industrial Chemistry, Bayero University, Kano Nigeria.

Exactly 2.74g and 4.95g of $Cd(NO_3)_2.4H_2O$ and $Ni(NO_3)_2.6H_2O$ were dissolved in to two separate 1 L volumetric flasks and made up to the mark with deionized water to make 1000 mg/L of Cd (II) and Ni (II) respectively. Working samples of 10, 15 and 20 mg/L concentrations were prepared by appropriate dilution of the stock solutions (Ben, 1992). pH adjustment where necessary, was achieved using 1.0 $molL^{-1}$ solution of HNO_3 and NaOH.

Collection and Preparation of Adsorbent

Mahogany (*swietenia macrophylla*) leaves were collected from G.R.A, Katsina in a plastic bag, and after being dried under shade they were cut into small pieces of about 5mm size. The plant particles were washed with tap water followed by deionized water, then filtered and finally dried at 65 °C for 24 hours. The solid adsorbent was pulverized and sieved to 212, 150, 106 μm mesh sizes, and the resulting powder fractions were preserved in plastic bottles for subsequently use

pH Adjustment of Adsorbate Solutions

The pH of the adsorbate solutions was kept to 4.5 to ensure minimal precipitation on the adsorbent surface, thus making the adsorption of charged metal ions more favourable (Greenwood and Earnshaw, 1997). The pH of the adsorbate solution was measured with a pH-meter (HI-98128) with automatic temperature compensation, and maintained at the proper value using nitric acid and sodium hydroxide.

Packing and Column Equilibration

A sintered column of 1 x 50 x 0.1 cm dimension was used to pack the adsorbent as slurry. Cotton wool was spread on top of the adsorbent to prevent its spillage on elution (Vasques *et al.,* 2009). This involves mixing the adsorbent with sufficient amount of deionized water in a beaker and poured into the column carefully. The stopcock was opened to allow the adsorbent to settle on gravitation and the lower meniscus of the water was kept just above the cotton wool to avoid letting the column run dry (Sen *et al.,* 2002). The column was operated at room temperature throughout the experimentation.

Adsorption Experiment

Exactly 10g of mahogany leaves were packed into a glass column and eluted with 250 mL of aliquot of 10 mg/L cadmium (II) solution. The pH was maintained at 4.5 and at a constant flow rate of 3 mL/min. Ten different fractions were collected in a well-labelled plastic bottles at 5

minutes time interval. The fractions were then taken for AAS measurements using 210-VGP spectrophotometer. In another run, different dosages (5, 10 and 15 g) of mahogany leaves powder were dry packed into different glass columns and eluted at the same condition of pH and flow rate as in the slurry experiment Residual concentrations of the fractions collected were determined in a similar way. Various initial concentrations 10ppm, 15ppm and 20ppm of Cd(II) and Ni(II) solutions were used in the adsorption process. The adsorption process was carried out using different particle sizes (212, 150, 106 μm) of mahogany leaves (ML) and the effect of particle size was studied (Galindo *et al.*, 2013; Nwabanne and Igbokwe, 2012). The whole experiment was conducted at room temperature.

The zero surface charge (pH_{pzc}) characteristics of ML powder was determined using the solid addition method (Cardenas-Pena *et al.*, 2012). Exactly 40 cm^3 of 0.1 mol/L NaCl solution was transferred to a series of 250 mL stoppered conical flasks. The initial pH (pH_i) values of the solutions were adjusted between 2 and 11 by adding either 0.1 mol/L HNO_3 and or 0.1 mol/L NaOH solutions. The total volume of the solution in each flask was exactly adjusted to 50 mL by adding NaCl solution of the same strength. The pH_i of the solutions was then accurately noted. 0.5 g of ML powder was added to each flask, and the flasks were securely capped immediately. The suspensions were then kept on intermittent shaking for 24 hours and allowed to equilibrate for 0.5 hour. The final pH (pH_f) values of the supernatant liquids were noted. The difference between the initial and the final pH values (ΔpH) was plotted against pH_i. The point of intersection of the resulting curve with abscissa, at which pH is zero, gave the pH_{pzc}. pH was measured on pH-meter (HI - 98128) (Cruz *et al.*, 2013).

PHYSICOCHEMICAL CHARACTERISTICS OF THE ADSORBENT

Attrition Loss: Attrition measures adsorbent's ability to withstand frictional forces by stirring and washing. It is an important parameter in understanding loss of adsorbent during handling and regeneration. A high attrition loss indicates that the adsorbents may be less effective and more expensive due to frequency of maintenance and purchase of additional material (Wuana *et al.*, 2015). Exactly 1.0 g of the adsorbent was dispersed in 100 mL of water and allowed to stand for 2 hours with constant stirring. After filtration, the residue was dried in an oven and weighed. The weight of the residue was then correlated to the original mass. Loss on attrition was calculated from equation (1) (Okafor *et al.*, 2015).

$$\text{Loss of attrition} = \left(\frac{M_i - M_f}{M_i} \right) \times 100 \qquad (1)$$

Where M_i and M_f are the initial and final masses of the adsorbent.

Moisture content: Exactly 2.0 g portion of the adsorbent was weighed and dried in an oven continuously at 45°C. The sample was constantly re-weighed at 10 mins time interval until a constant weight was obtained. The ratio of weight change to the original weight expressed in percentage gives the moisture content (Okafor *et al.*, 2015).

Bulk density: The bulk density of the adsorbent was determined by tapping procedure

$$\text{Bulk density} \left({}^{g}\!\!\diagup\!\!{}_{Ml} \right) = \frac{W_{ads}}{V_{ads}} \qquad (2)$$

Where W_{ads} is the weight of adsorbent (g) and V_{ads} is the volume of adsorbent (mL).

Bulk density is an important characteristic of adsorbents as it is a measure of the amount of adsorbate the adsorbent (mahogany leaves) can hold per unit volume. It is a useful property that gives an idea of the volume activity of the adsorbents, and it depends on the starting material (Shah *et al.*, 2010).

Pore (Void) Volume: Exactly 2.0 g portion of the adsorbent (mahogany leaves powder) was immersed in a 30 mL distilled water and boiled for 25 minutes to displace air contained in the pores after which the sample was retrieved from the water and re-weighed. The sample was superficially dried on a filter paper. The increase in weight per unit mass of the sample divided by the density of water gave the pore volume (Nurul'ain, 2007).

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB}C_o t - k_{AB}N_o \frac{Z}{F} \qquad (3)$$

Where C_o and C_t (mg/L) are the inlet and effluent dye concentrations, respectively; k_{AB} (L/mg min) is the Adams-Bohart rate constant, F (cm/min) is the linear velocity. F value is calculated by dividing the flow rate by the column cross sectional area, Z (cm) is the bed depth of column, and N_o (mg/L) is the saturation concentration.

Yoon–Nelson Model.

The Yoon and Nelson model is considered the less complicated column model as it requires no

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN}t - k_{YN}\tau \qquad (4)$$

Where K_{YN} is the Yoon and Nelson rate constant (min^{-1}), C_o is the inlet or initial concentration (mg/L), C_t is the effluent dye concentration (mg/L), t is the breakthrough (sampling) time (min) and τ is the time required for 50% adsorbent breakthrough (min).

(Okafor *et al.*, 2015). Exactly 5.0 g portion of the adsorbent which was dried at 110°C for an hour was packed into a 100 mL measuring cylinder. The bottom of the cylinder was tapped gently on the laboratory bench top several times until there was no further diminution of the sample level. This procedure was repeated twice and the average result recorded. The bulk density was then calculated using equation (2).

FTIR and SEM of the Stationary Phase: Organometallic compounds contain ligands that bond to metal atoms or ions through carbon bonds. Fourier Transform Infrared (FTIR) (Carry 630) and Scanning Electron Microscopy (SEM) (Phenom ProX) were used to observe the surface physical morphology of the adsorbent before and after adsorption (Vieira *et al.*, 2014).

Mathematical Model of the Adsorption Column Adams Bohart Model

The Adams–Bohart model (Bohart and Adams, 1920) assumes that the adsorption rate is proportional to both the residual adsorbent capacity and the concentration. This model is used for the description of the initial part of the breakthrough curve. The Adams–Bohart model can be expressed using equation (3) (Ahmad and Hameed 2010).

detailed data concerning the characteristics of adsorbent, the type of adsorbent and the physical properties of adsorption bed. The assumption of this model is based on the rate of decrease in the probability of adsorption for each adsorbent molecule, is proportional to the probability of adsorbent adsorption and the probability of adsorbent breakthrough on the adsorbent. For a single component system, the Yoon and Nelson equation is expressed in its linear form by equation (4) (Yoon and Nelson, 1984).

RESULTS AND DISCUSSION

Adsorption or removal of cadmium and nickel from solutions of their ions with mahogany leaves powder was carried out using dynamic adsorption.

Physicochemical Characteristics of Mahogany Leaves

The physicochemical characteristics of mahogany leaves adsorbent are recorded in Table 1. Mahogany leaves showed 17% attrition loss indicating its hardness or resistance to abrasion. The value helps to achieve more effective adsorption. This value is higher than 12.5% obtained for *Moringa Oleifera* (Wuana *et al.*, 2015) and less than 40.26% for bituminous coal (Qureshi *et al.*, 2007).

Moisture content suggests extensive porosity in the structure of the adsorbents. It has been observed that if the moisture content of adsorbent is high, its adsorptive capacity will be reduced (Sugunadevi *et al.*, 2002). The moisture content of mahogany leaves was found to be 5.2.0%, this value is higher than 1.64%, 1.34%, and 1.50% for *Recinius communis* Linn, *Carica papaya* Linn and *Morida pubescence* activated carbons (Kathikeyan and Ilango, 2008) respectively. The value is lower than 5.22%, 19.5%, 7.18% and 7.21% obtained for *vitellaria paradox* (shea nut) shell, fluted pumpkin, apricot stone and almond shells (Jimoh *et al.*, 2015; Ekpete *et al.*, 2010).

The bulk density of 268 kg/m³ was recorded for mahogany which is higher than the minimum requirement of (250 kg/m³) for application in removal of pollutants from waste water (Agrawal and Bajpai, 1991). This value is higher than 178 kg/m³ and 142 kg/m³ reported for *moringa oleifera* pod husks and *gmelina arborea* saw dust activated carbions (Wuana *et al.*, 2015; Ogunsile *et al.*, 2014), but less than 560 kg/m³ 630 kg/m³ reported for maize cobs and coconut shell (Akporhonor and Egwaikhide, 2007; Amuda and Ibrahim, 2006).

The pore or void volume of 1.10 cm³/g was recorded for mahogany leaves which is higher than 0.728 cm³/g reported for olive stones (Bohli *et al.*, 2012), but lower than 1.23 cm³/g reported for maize cob (Okafor *et al.*, 2015).

Table 1: Physicochemical Characteristics of Mahogany leaves

Characteristics	Mahogany leaves
Total Pore (void) volume (cm³/g)	1.10 ± 0.01
Attrition test (%)	17 ± 0.0
Moisture content (%)	5.2 ± 0.0
Bulk density (kg/m³)	268 ± 1.0

Effect of Contact Time

The result showed that the initial concentration of cadmium decreased from 10 to 1.375 mg/L after 5 minutes, 0.625 mg/L after 40 minutes and only 0.375 mg/L after 50 minutes as shown in Figure1. Similar result was obtained for the removal of nickel using same adsorbent, Figure 2. This implies that, increase in contact time decreases the concentration of the metal. This is due to the longer time the adsorbate spends with the adsorbent before draining out. El-Kamash A. (2008) reported a similar result that, increase in contact time decreases the concentration of the adsorbates (Cs^+ and Sr^{2+}). Similar result was also reported by Mustapha *et al.*, (2014).
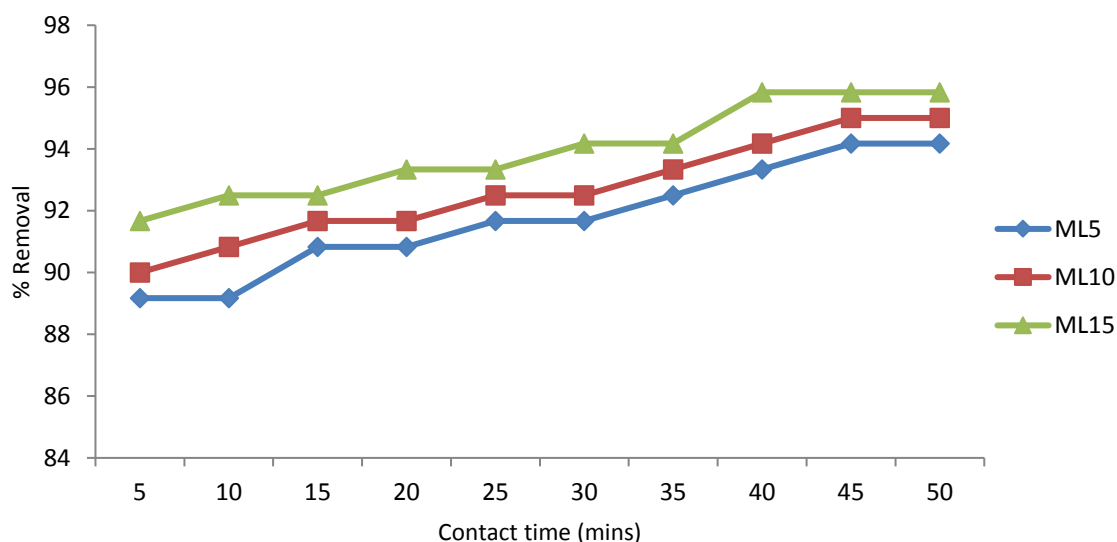

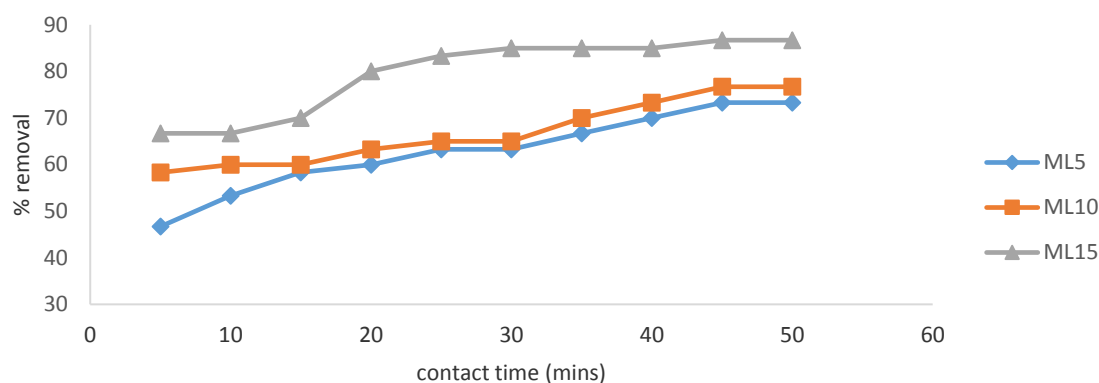**Fig. 1: Effect of contact time and adsorbent (ML) dose for the removal of Cd(II) ion**

Fig. 2: Effect of contact time and adsorbent (ML) dose for the removal of Ni (II) ion

Effect of Adsorbent Dose (g)

The result showed that, the percentage removal after 5 minutes using 5 g of mahogany was 89.17; by using 10 g of ML was 90%, but up to 91.5% using 15 g of the adsorbent (Figure 1). Similar result was obtained for the removal of nickel using same adsorbent, Figure 2. The decrease in adsorption capacity for lower adsorbent weight may be due to the decrease in total adsorption surface area available resulting from overlapping or aggregation of adsorption sites (Boota *et al*., 2009).

Effect of Initial Metal Ion Concentration (C_o)

Adsorbent shows a more significant percentage removal at high concentrations of heavy metals. This is attributed to the increase in the number of metal ions competing for available binding sites on the adsorbent at higher concentration levels (Abasi *et al*., 2011; Ibrahim and Jimoh, 2011). At low concentration, saturation of adsorbent by Cd (II) and Ni (II) ions could not be achieved, as the number of metal ions was smaller than the number of binding sites present on the adsorbent. Consequently, increasing the concentration of metals ions in the solution is expected to result in increase in metal uptake until saturation of adsorbent is attained (Zubair *et al*., 2008). A significant increase in percentage removal was observed as the concentration of cadmium is increased from 10 to 20 mg/L, Figure 3. Similar result was obtained by increasing the initial concentration of nickel from 10 to 20 mg/L, Figure 4.
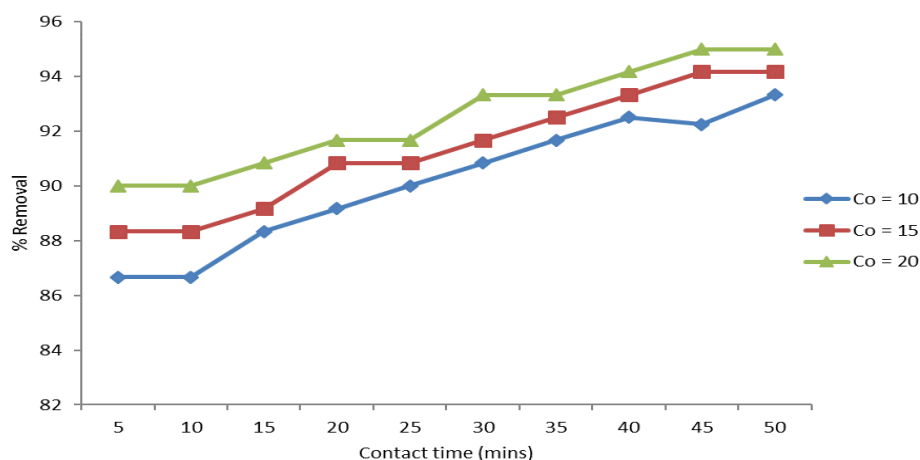

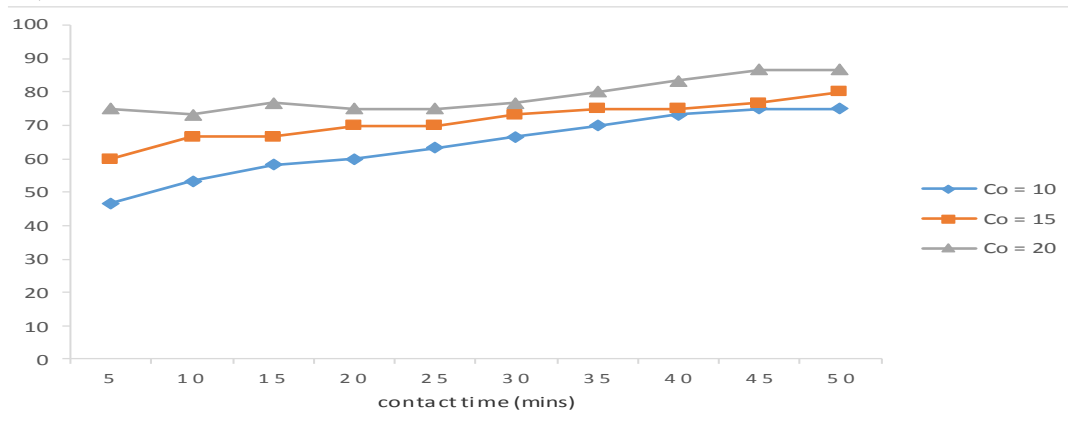**Fig. 3: Effect of initial concentration (mg/L) of Cd (II) ion**

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Fig. 4: Effect of initial concentration (mg/L) of Ni (II) ion

Effect of Particle Size

Among the three different particle sizes (212, 150, 106 μm), the smaller particle size 106 μm, was found to be more effective towards the removal of cadmium and nickel ions (Figure 5).

The smaller particle size of the adsorbents showed better removal efficiency due to increase in surface area. The larger the surface area, the higher the adsorption sites and the better will be the adsorption capacity (Saraswat and Rai, 2009).
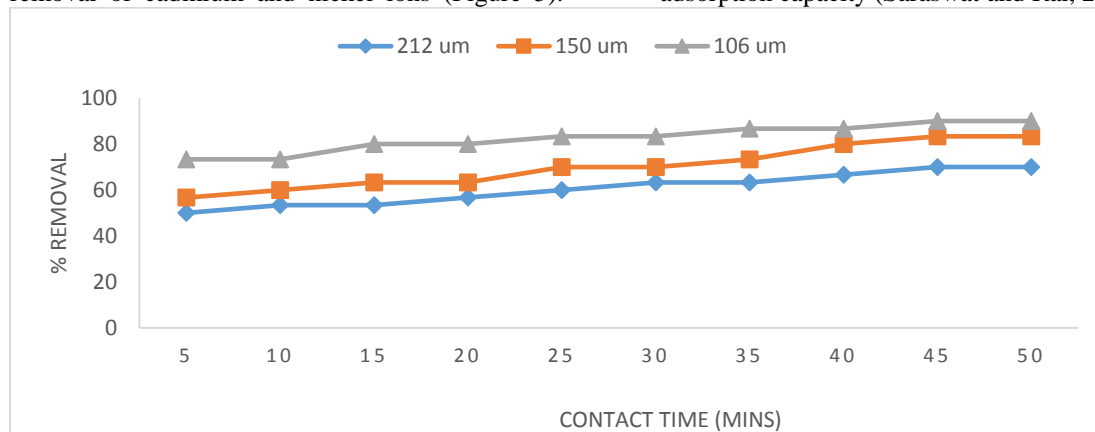

Fig. 5: Effect of particle size of the Stationary Phase (ML 10g)

Effect of pH of zero charge (pH$_{pzc}$)

The pH$_{pzc}$ of the adsorbent was found to be 7.8, (Figure 6) indicating weakly basic material.
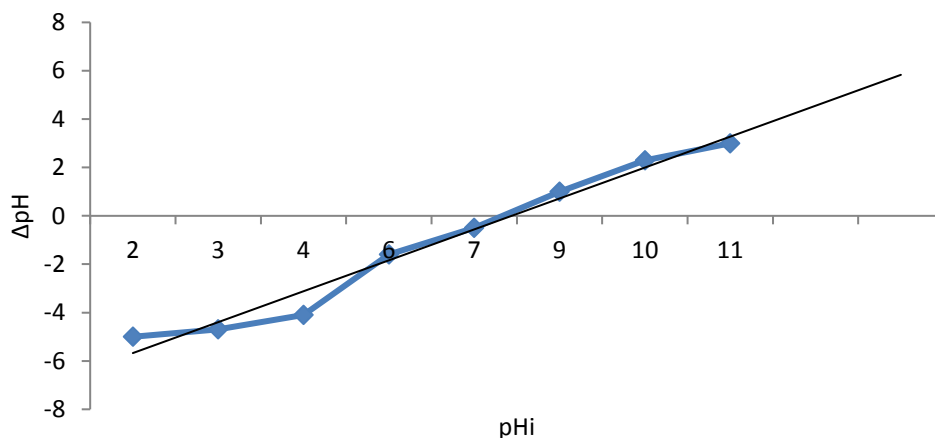

Fig. 6: Effect of pH of zero charge (pH$_{pzc}$) of ML

FTIR Characteristics of Derived and Spent Adsorbent: From Fig. 7, FMLP, the

adsorption bands at 1026.70, 1078.44, 1157.63 and 1244.62 cm^{-1} were as a result of C-O stretching,

1716.85 and 1733.86cm^{-1} were due to C=O stretching, 2925.33cm^{-1} due to C-H stretching and 3420.87cm^{-1} due to O-H stretching in the structures of the organic compounds present in the leaves, such as swietenolide monohydrate. Fig. 8, ML loaded with Cd (II), the adsorption band 1436cm^{-1} was due to Cd-aromatic ring stretching indicating that the adsorbent was effective. Fig. 9, ML loaded with Ni (II), the adsorption bands at 659 and 1439

cm^{-1} were due to Ni-OH stretching and Ni-aromatic ring stretching respectively; 1318 cm^{-1} due to COO group of carboxylic acid salt, thus indicating that the adsorbent is effective in removing the metal. Therefore, it can be concluded that, the functional groups which can bind the metal ions are the type –OH, -NH, C=N, -C-O and –COO (Vieira *et al.*, 2014; Stuart, 2004).
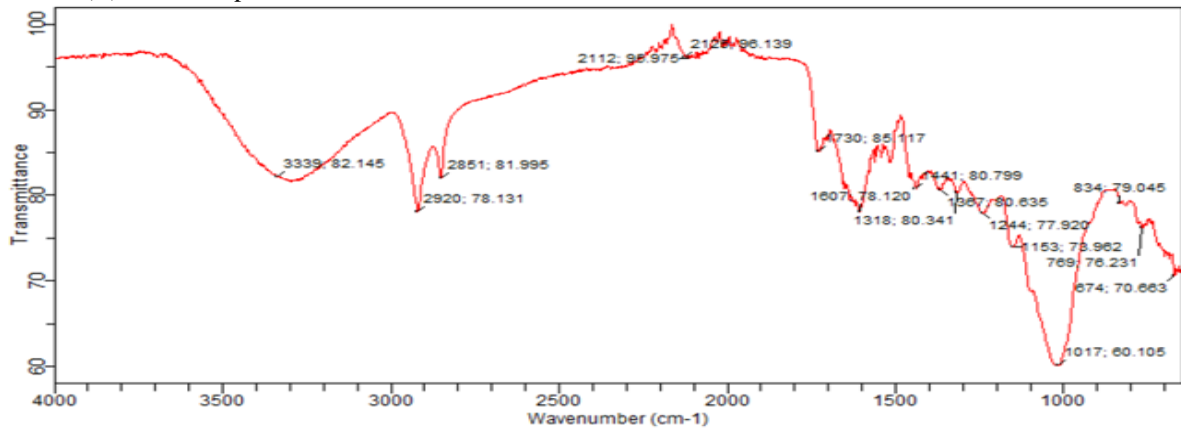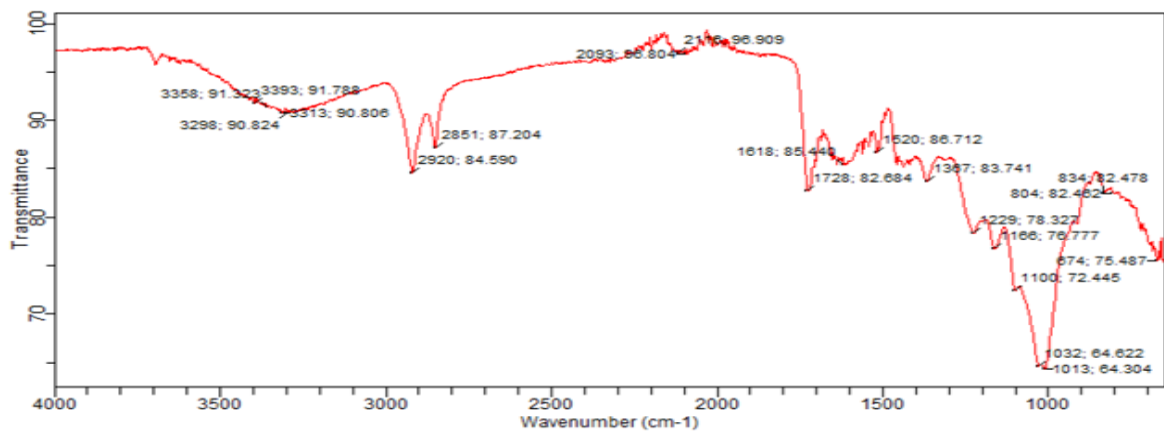

Figure 7: FTIR of unloaded ML

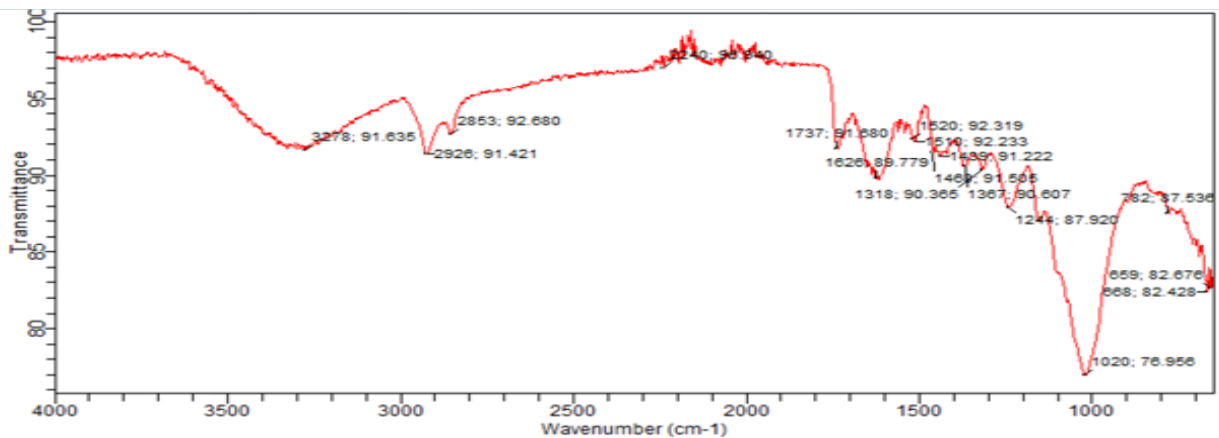

Figure 8: FTIR of ML loaded with Cd (II)

Figure 9: FTIR of ML loaded with Ni (II)

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Table 2: FTIR of the Stationary Phase

Unloaded Mahogany leaves		Mahogany Leaves + Cd		Mahogany Leaves + Ni	
V (cm^{-1})	Functional group	V (cm^{-1})	Functional group	V (cm^{-1})	Functional group
3420.87	O – H, N – H	3447	O – H, N - H	3278	O – H, N - H
2925.33	C - H	2924	C - H	2926	C - H
1733.86	C = O	1734	C = O	1737	C = O
1696.92	C - N	1647	C – N	1626	C = C
1636.40	C = C	1636	C = C	1439	M – Ar
1339.30	ArC - N	1437	M – Ar	782	= C – H
1026.70	C - O	1318	COO	1318	COO
767.37	= C - H	1374	ArC - N	668	C – Cl
-	-	1339	C = O	659	M – C
-	-	1027	C – O	3278	O – H, N - H
-	-	652	M - C	2926	C - H

Scanning Electron Microscopy of Derived and Spent Adsorbent: Figure 10, presents SEM micrograph of unloaded ML; Figure11 presents SEM micrograph of ML loaded with Cd. SEM micrograph of mahogany leaves indicated that the surface was highly irregular and porous in nature. The fibrous-shaped cellulose skeleton is visible (Naiya *et al*., 2009). According to Tarley and Arruda (2004), the morphology of the adsorbent can facilitate adsorption of metals in different parts of the material. Based on the mapping of metals in the micrographs performed by EDX it is possible to observe a uniform distribution of the metallic ions, but cadmium was not observed due to high concentration of silicon (Perkin- Elmer, 2008). Therefore, based on the morphology and on the fact that a higher concentration of silica is present in the outer epidermis of the ML, one can conclude that this material presents a morphological profile with the capability to retain metal ions.
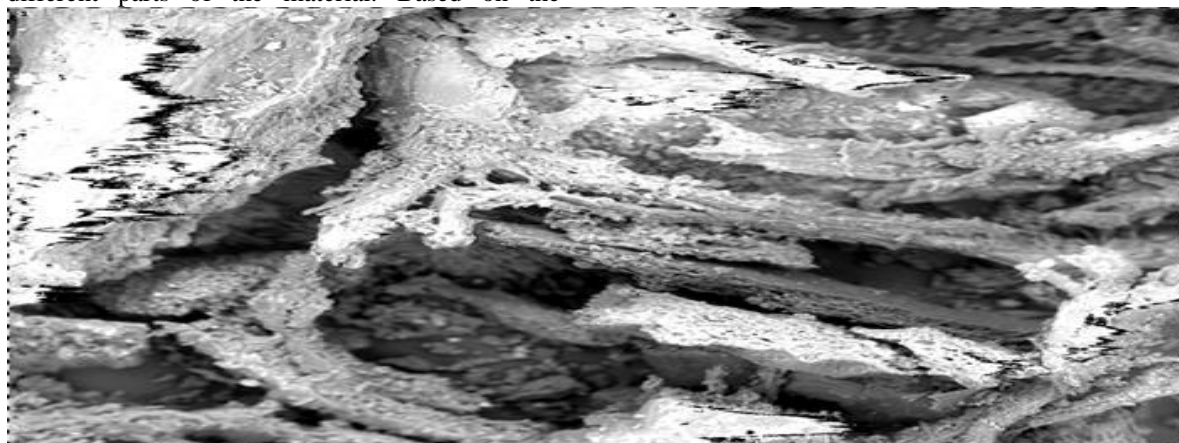
Fig.10: SEM of unloaded Mahogany leaves
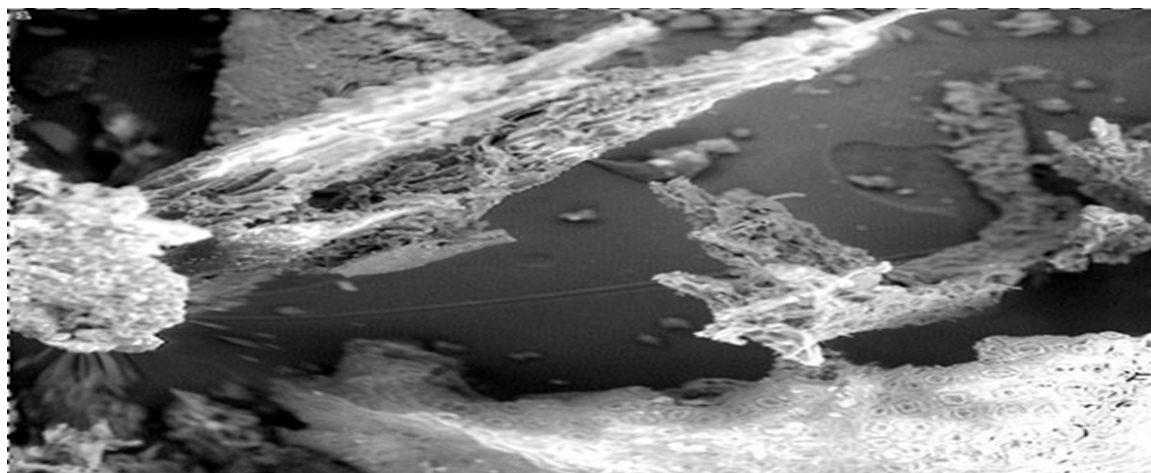
Fig. 11: SEM of Mahogany leaves loaded with Cd (II)

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Modelling of Fixed-Bed Column Breakthrough: Various kinetic and mass transfer models have been developed to predict the dynamic behaviour of the column. These models have been utilized to determine breakthrough performance and also to calculate the column kinetic parameters and adsorption capacity of the fixed-bed column (Sen *et al*., 2014). Adams-Bohart model, the break through curve (BTC) for Cd (II) shown in Figure 5.

But for Yoon-Nelson model, the BTC for Cd (II) is shown in Figure 6. Table 8 shows the parameters of the models for mahogany.

Adams-Bohart model: The values of k_{AB} and N_0 can be obtained from the slope and intercept, respectively, of a linear plot of ln (C_o/C_t) against t for Cd (II) and Ni (II) as shown in Figure 12 and 13 respectively.
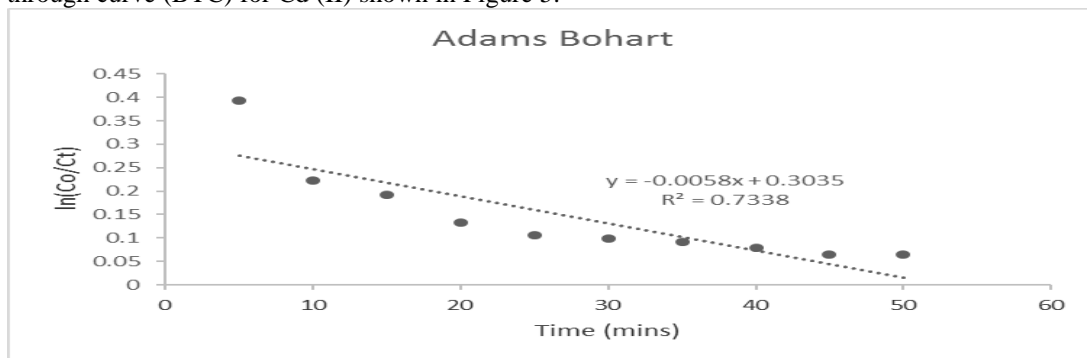

$$y = -0.0058x + 0.3035$$
$$R^2 = 0.7338$$

Fig. 12: Adams-Bohart Model Plot for Cd (II)

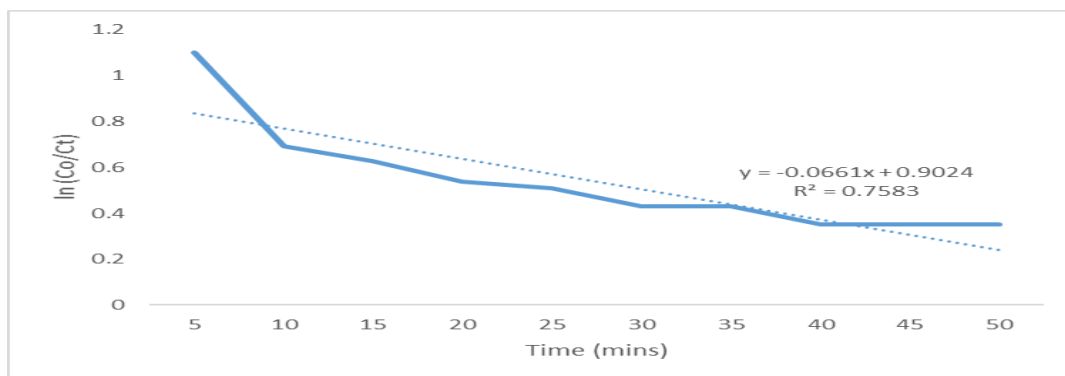$$y = -0.0661x + 0.9024$$
$$R^2 = 0.7583$$

Fig. 13: Adams-Bohart Model Plot for Ni (II)

Yoon-Nelson model: The plot of ln $[C_t/(C_0 − C_t)]$ vs. sampling time (t) will give a straight line with

slope of K_{YN} and intercept $K_{YN} \tau$ for Cd (II) and Ni (II) as shown in Figure 14 and 15 respectively.
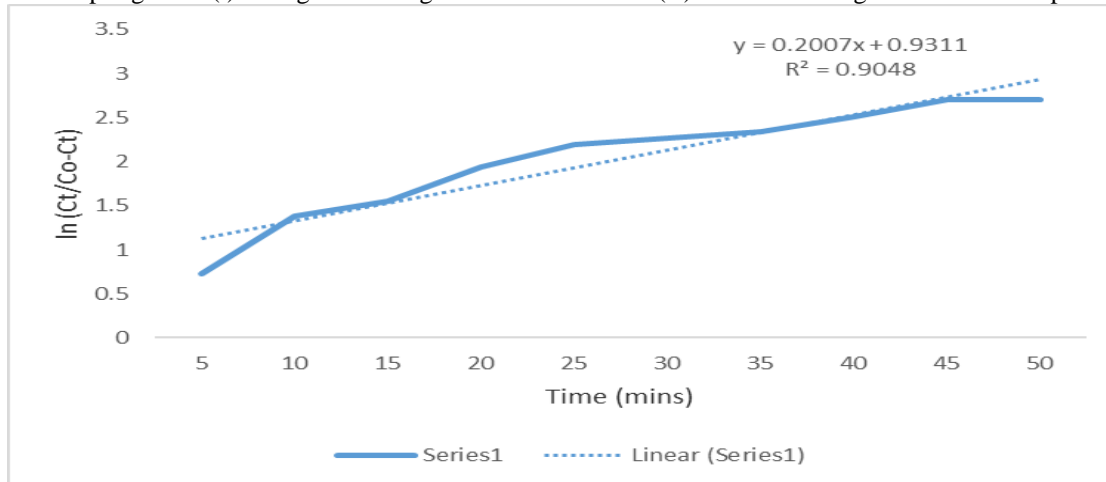

$$y = 0.2007x + 0.9311$$
$$R^2 = 0.9048$$

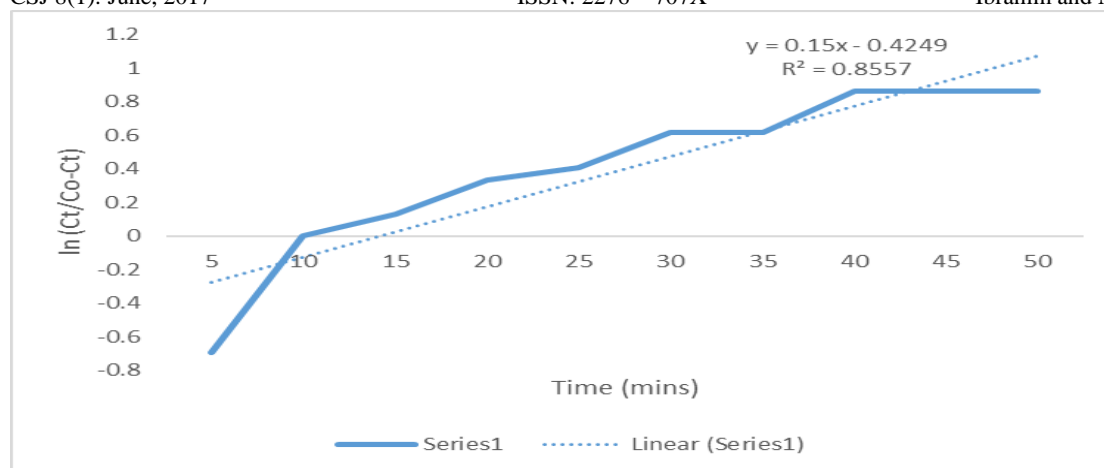**Fig. 14: Yoon-Nelson Model Plot for Cd (II)**

Fig. 15: Yoon-Nelson Model Plot for Ni (II)

Table 4: Adams – Bohart and Yoon – Nelson Parameters for Cd (II) and Ni (II) ions

*Adams-Bohart Parameters	Cd (II)	Ni (II)
K_{AB} (L/min mg)	5.8×10^{-3}	6.61×10^{-2}
N_0 (mg/l)	0.3035	0.9025
R^2	0.7338	0.7583
*Yoon-Nelson Parameters		
K_{YN} (min^{-1})	0.2007	0.15
τ (min)	4.64	2.83
R^2	0.9048	0.8557

The adsorption process can be explained using Adams-Bohart and Yoon–Nelson models, even though the values of correlation coefficient R^2 were not high in the former. This signifies better linearity between the data for both Cd and Ni in Yoon-Nelson model as shown in Table 4.

CONCLUSION

The positive results obtained from this research showed that, mahogany leaves are efficient for the removal of cadmium and nickel. Factors such as contact time, adsorbent dosage, initial concentration, particle size and the pH point of zero charge influenced the adsorption process. The pH point of zero charge was found to be 7.8, within basic region. The pH of the adsorbate solution was kept to 4.5 to ensure minimal precipitation on the adsorbent surface, thus making the adsorption of charged metal ion more favorable. Physicochemical characteristics, such as attrition loss, void volume, surface area, bulk density of the adsorbent show a positive result, indicating that the adsorbent is effective for the removal cadmium. FT-IR and SEM (with EDX) analysis also showed that mahogany leaves have the capability to remove cadmium (II) and nickel (II) from the solutions of their ions.

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