

# Adsorption of Cadmium (II) ion From Aqueous Solution Using Activated Carbon Produced from Oil Bean Seed Shell

J. N. Aningo

Department of Chemical Engineering  
Enugu State University of Science and  
Technology, Enugu, Nigeria  
aningoamaka@yahoo.com

T. O. Chime, C.O. Nevo

Department of Chemical Engineering  
Enugu State University of Science and  
Technology, Enugu, Nigeria  
Chimetom@yahoo.com

**Abstract**— In this study, the use of activated carbon produced from oil bean seed shell to remove Cd (ii) from aqueous solution was investigated under batch mode. The characterization result showed that the adsorbent has a high surface area of 295m<sup>2</sup>/g, this must have contributed to the high adsorption capacity of the adsorbent. The FTIR analysis was used to identify the functional groups likely to participate in metal binding. SEM analysis was also carried out on the raw sample and its activated carbon. The effect of time, pH and adsorbent dose were investigated. The isotherm data followed both the Langmuir and Freundlich models satisfactorily with R<sup>2</sup> values of 0.92 and 0.97 respectively. The maximum monolayer adsorption capacity is 34.448mg/g. Kinetic data did not follow any of the two models used. The positive value of  $\Delta H^\circ$  and  $\Delta S^\circ$  (13610kJ/mol and 45.253J/molK) respectively, indicate an endothermic, spontaneous adsorption process. The results of this work indicate that the activated carbon produced from oil bean seed shell can effectively serve as low cost adsorbent for the removal of Cd (ii) ion from wastewater.

**Keywords**— Oil bean seed shell, adsorption, activated carbon, carbonization, activation

## I. INTRODUCTION (Heading 1)

Presently, there is excessive release of wastewater into the environment. This is due to rapid growth in population, industrialization, urbanization, technological advancement, energy utilization etc. Some wastes are also generated from different homes and are released into the environment. Environmental pollution is high in developing countries like Nigeria, where there are no strict laws guiding the discharge of waste.

Heavy metals like cadmium, copper, chromium, lead, arsenic, nickel, are some of the heavy metals that are generated from the many industries and homes that exist globally. The treatment of these wastewaters is the major challenge facing these industries, since these heavy metals cause different health problems when accumulated in the human bodies through numerous means.

Cadmium mainly accumulates in the kidneys and livers, hence leading to kidney failure, renal stone formation, bone disease and persistent proteinuria as a sign of kidney damage. Other effects from cadmium exposures may include muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shocks, renal failure (Igbal et al, 2007).

Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption and co-precipitation/ adsorption. Studies on the treatment of effluent bearing heavy metals have revealed adsorption to be a highly effective technique for the removal of heavy metals from waste stream and activated carbon has been widely used as an adsorbent (Chand et al, 1994). The adsorption technique has been found to be one of the most effective methods for the removal of metal ions from solution.

The objective of this study is to remove cadmium from aqueous solution using activated carbon produced from oil bean seed shell (low cost adsorbent). The SEM and FTIR analysis of the adsorbent was carried out. Isotherm, Kinetics and Thermodynamic parameters were determined.

## II. MATERIALS AND METHODS

### Material:

Dried sample of oil bean seed (*Pentaclethra macro benth*) shell, Cadmium (ii) trioxonitrate (v), distilled water, NaOH, HCl, Whatmann filter paper.

### Equipment:

Weighing balance (electronic), loading balance, electric oven, electric furnace, shaker, locally fabricated hydrolysis reactor with thermocouple, spectrometer, pH Meter, atomic adsorption spectrophotometer (AAS).

### Production of activated carbon

#### Preparation of activated carbon from oil bean seed shell

The oil bean seed shell was collected from Abakpa Nike Enugu, Enugu state, Nigeria. It was washed, dried and crushed to desired mesh size (1- 2 $\mu$ m). It was carbonized at 800°C for 2hrs in a stainless steel vertical

tubular reactor placed in a tubular furnace. The char produced was crushed and sieved with 600µm sieve size. The char was soaked in 6M KOH solution with (1:5) char to KOH ratio. The mixture was then dehydrated in an oven at 105°C to remove moisture and then was activated under the same condition as carbonization, but to different final temperature of 850°C for 1hr. The activated product was then cooled to room temperature and washed with hot deionized water and 0.1N HCl until pH of 6-7 was obtained.

### Preparation of aqueous solution (heavy metal solution)

All the reagents used for this study were of Analar grade from Cornraws Nigeria limited, Enugu, Nigeria. Stock metal solutions of 1gl<sup>-1</sup> of Cd (II) as Cadmium (ii) trioxonitrate (v) (Cd(NO<sub>3</sub>)<sub>2</sub>) was prepared. The desired concentration was prepared through the adequate dilution of stock solution with distilled water. The initial pH was adjusted using 1M HCl or NaOH. Initial metal concentrations were measured using Shimadzu atomic adsorption spectrophotometer (Buck scientific model 210VGP).

### Characterization of Activated Carbon

The Characterization of adsorbent was carried out to determine some properties of the adsorbent. The surface area of the adsorbent was determined using standard procedure (Foo and Hameed, 2012). The acidic and basic sites on the adsorbent were determined by the acid-base titration method (Ofomaja,2011). The volatile matter content was determined using the method posed by (Onwu, 1999). The ash content, bulk density, and carbon content were determined using standard procedure. The pH of the activated carbon was determined using standard test method (Ekpete and Horsfall, 2011). The thermal drying method was used to determine the moisture content of the sample. Determination of the iodine content was done using the procedure described by (Gimba and Musa, 2007). Fourier-transform infrared spectrophotometer (FTIR; Shimadzu 8400s) was used to identify the functional groups responsible for binding of heavy metal ion, while the scanning electron microscopy (SEM; Hitachi S4800) was used to study the surface morphology of the adsorbent.

### Batch Adsorption Experiment

The activated carbon produced was crushed and sieved with 250µm mesh size, before using it for the experiment. The batch adsorption studies were carried out at room temperature. Batch mode was chosen because of its simplicity. The batch experiment was performed by adding 0.3g of the adsorbent to 30ml of metal solution in 60ml plastic container at room temperature. The effect of temperature was determined by placing the plastic bottle in a thermo- stated water bath. The effects of operating parameters were carried out on pH, adsorbent dose, initial metal ion concentration, and contact time. Each experiment was carried out twice, and the average value calculated to

minimize error. The amount of metal ion adsorbed was calculated from the equation below:

$$q_e = V \frac{(C_o - C_e)}{m} \dots\dots\dots (1)$$

$$\% \text{ Adsorption} = 100 \times \left[ \frac{C_o - C_e}{C_o} \right] \dots\dots\dots (2)$$

q<sub>e</sub> (mg/g) is the adsorption capacity of adsorbent on the adsorbate at equilibrium. C<sub>e</sub> (mg/l) and C<sub>o</sub> (mg/l) are the equilibrium concentration and initial concentration of the metal ions in solution respectively. V (L) is the volume of solution and m (g) is the mass of the adsorbent used.

### Adsorbent Dose

The effect of adsorbent dose was carried out by varying the amount of adsorbent used. 30ml of the metal solution was treated using different doses of the activated carbon (ie 0.1 – 0.5g). The samples were agitated for 60mins and at constant pH, initial concentration, and temperature. It was filtered at the end of the given contact time and analysed using AAS.

### Contact time

The effect of contact time was studied by adding 0.3g of the adsorbent to 30ml of metal solution in 60ml plastic bottle. The sample was agitated at varying time intervals of (10-90mins) after which the samples were withdrawn, filtered and analyzed. Experiments were conducted at constant temperature, pH, and initial metal ion concentration.

### pH of Solution

The effect of pH was performed by varying the pH values from 2-8 using dilute NaOH/ HCl solutions. Every other condition was kept constant. The samples were agitated for 60mins, filtered and analysed using AAS.

### Initial metal ion concentration

The effect of initial metal ion concentration was carried out at 300mg/l, 240mg/l, 160mg/l, and 80mg/l. Other parameters were kept constant.

### Adsorption Isotherm Studies

Adsorption isotherms were used to relate the adsorbate concentration in solution and the amount on the adsorbent at equilibrium (Ayranci and Duman, 2005). The batch isotherm studies were carried out by mixing 0.3g of the adsorbent with 30ml of the metal solution at varying concentrations of 80mg/l, 160mg/l, 240mg/l, and 300mg/l. The samples were agitated for 60mins, withdrawn from the shaker, filtered and analyzed. The adsorption capacity at equilibrium and the percentage adsorption were calculated. The results gotten were fitted to Langmuir, Freundlich, Tempkin, and Dubinin- Radushkevich isotherm models.

### Langmuir isotherm model:

Langmuir isotherm model is expressed as (Akpomie and Dawodu, 2014):

$$\frac{C_e}{q_e} = \frac{1}{q_L K_L} + \frac{C_e}{q_L} \dots\dots\dots(3)$$

Where  $q_l$  (mg/g) is monolayer adsorption capacity of the adsorbent and  $K_L$  (L/mg) is the adsorption constant which reflects the affinity between the adsorbent and adsorbate.  $q_L$  and  $K_L$  were determined from the slope and intercept of the plots of  $C_e/q_e$  versus  $C_e$ . An essential feature of the Langmuir isotherm can be expressed in terms of dimensionless separation factor (RL) defined as:

$$RL = \frac{1}{[1+K_L C_0]} \dots\dots\dots(4)$$

**Freundlich isotherm model:**

The Freundlich isotherm is based on the assumption that sorption takes place on homogeneous adsorbent surface, where the sorption energy distribution decreases exponentially and can be expressed as:

$$\text{Log } q_e = \text{Log } KF + \left[\frac{1}{n}\right] \text{Log } C_e \dots\dots\dots(5)$$

Where  $KF$  (mg/g)(mg/l)<sup>1/n</sup> and  $n$  are constants for adsorption capacity and intensity respectively. A plot of  $\text{Log } q_e$  versus  $\text{Log } C_e$  gives a straight line graph of slope  $1/n$  and intercepts  $\text{Log } KF$ .

**Tempkin isotherm model:** This is based on the assumption that the free energy of adsorption is a function of the surface coverage, it is expressed as:

$$q_e = B \ln A + B \ln C_e \dots\dots\dots(6)$$

Where  $B = \frac{RT}{b}$  (mg/g) is the isotherm constant related to the heat of adsorption, and  $A$  (L/g) is the equilibrium binding constant corresponding to the maximum binding energy,  $R$  is the gas constant (8.314J/molk<sup>-1</sup>) and  $T$ (k) is the absolute temperature. The constants  $A$  and  $B$  were calculated from the plot of  $q_e$  and  $\ln C_e$ .

**The Dubinin – Radushkevich isotherm**

This isotherm assumes a homogeneous surface or a constant adsorption potential and it is expressed as:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \dots\dots\dots(7)$$

Where  $q_m$  (mg/g) is the theoretical saturation capacity,  $\beta$  (mol<sup>2</sup> /j<sup>2</sup>) is a coefficient related to the mean free energy of adsorption and  $\epsilon$  is the Polanyi expressed as:

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \dots\dots\dots(8)$$

The constant  $q_m$  and  $\beta$  were calculated from the intercept and slope of  $\ln q_e$  versus  $\epsilon^2$ .

**Adsorption Kinetics Studies**

The batch adsorption studies were carried out at varying time intervals and were fitted to the Pseudo-first-order and Pseudo –second –order equations. The linear form of the Pseudo –second – order is given as:

$$\text{Log } (q_e - q_t) = \text{Log } q_e - \left(\frac{K_1 t}{2.303}\right) \dots\dots(9)$$

Where  $K_1$  (min<sup>-1</sup>) is the rate constant and  $q_t$  and  $q_e$  are the amounts of metal ion adsorbed at time  $t$  and equilibrium respectively. The constant  $K_1$  and  $q_{e,cal}$  were obtained from the slope and intercept of the plot of  $\text{Log } (q_e - q_t)$  versus  $t$ .

The pseudo –second – order model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Akpomie and Dawodu , 2014). The linear form of the pseudo-second –order equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots(10)$$

$K_2$  (g/mgmin) is the rate constant. The initial sorption rate  $h$  was calculated from the equation:  $h = K_2 q_e^2$ . If the pseudo –second –order equation is applicable, the plot of  $t/q_t$  versus  $t$  yields a straight line graph.  $K_2$  and  $q_e$  were to be calculated from the slope and intercept of the plot respectively.

**Thermodynamics Studies**

To carry out the thermodynamics studies, experiments were performed by mixing 0.3g of the adsorbent with 30ml of the metal solution at varying temperatures of 303k, 313k, 323k, and 333k. A constant initial concentration of 250mg/l and contact time of 60mins was maintained. The samples were agitated for 60mins, withdrawn from the shaker, filtered and analyzed.

Equilibrium adsorption capacity and the percentage adsorption were calculated from the values gotten.

Thermodynamic parameters such as standard free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S$ ) were calculated with the following equations (Bhattacharrya and Gupta, 2000).

$$K_c = \frac{C_a}{C_e} \dots\dots\dots(11)$$

$$\Delta G = -RT \ln K_c \dots\dots\dots(12)$$

$$\ln K_c = - (\Delta H^\circ / RT) + (\Delta S^\circ / R) \dots\dots(13)$$

Where  $K_c$  is the thermodynamic equilibrium constant,  $C_a$  (mg/l) is the concentration of metal ions adsorbed at equilibrium ,  $C_e$  (mg/l) is the concentration of metal ions remaining in solution at equilibrium,  $R$  is the ideal gas constant (8.314j/molk) and  $T$ (k) is the absolute temperature. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  will be gotten from the slope and intercept of the plot of  $\ln K_c$  versus  $1/T$ .

**RESULTS AND DISCUSSION**

Table 1: Results of characterization of raw oil bean seed shell and its activated carbon.

S/N	UNIT	PARAMETERS	VALUES
-----	------	------------	--------



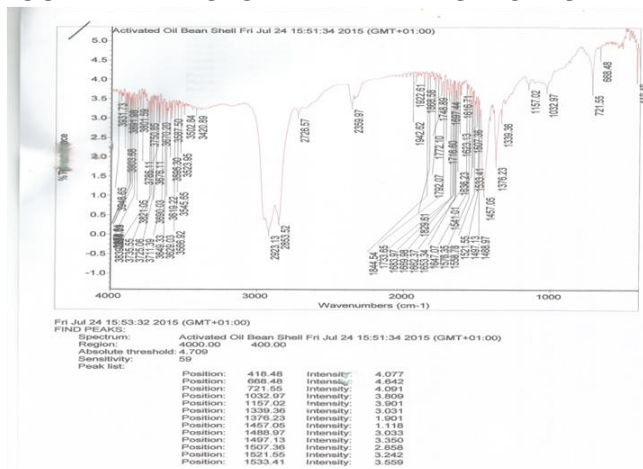
			Raw sample	Activated carbon
1	g/ml	Bulk Density	0.650	0.974
2	%	Ash Content	9.0	3.0
3	%	Moisture content	4.0	1.0
4	%	Iodine number	0.73	0.70
5	%	pH	6.7	7.08
6	m <sup>2</sup> /g	Surface Area	205.4	295
7	%	Volatile matter	70.8	31.8
8	%	Fixed Carbon	16.2	64.2

From the table 1 above, it can be observed that the activated carbon produced is at neutral pH i.e. 7.

The specific surface area of an adsorbent is important in determining its adsorption capacity, and a high value is desirable for optimum adsorption. In general, the higher the specific surface area of a material the higher its adsorption potential and vice versa, although not in all cases (Akpomie and Dawodu, 2014). From the table 1, the surface area of raw oil bean seed shell is 205.4m<sup>2</sup>/g which was increased to 295m<sup>2</sup>/g after carbonization and activation.

The slurry pH and the pH<sub>pzc</sub> of adsorbents usually give information about surface oxygen complexes and the electronic surface charge of an adsorbent arising from the interaction between the adsorbent surface and aqueous solution. The complexes on adsorbent surfaces are generally classified as acidic, basic or neutral (Akpomie and Dawodu, 2014). The pH in the above table indicates that the adsorbent (Activated oil bean seed shell carbon) is neutral (pH of 7), but was slightly acidic before carbonization and activation.

#### FOURIER TRANSFORM INFRARED SPECTRUM



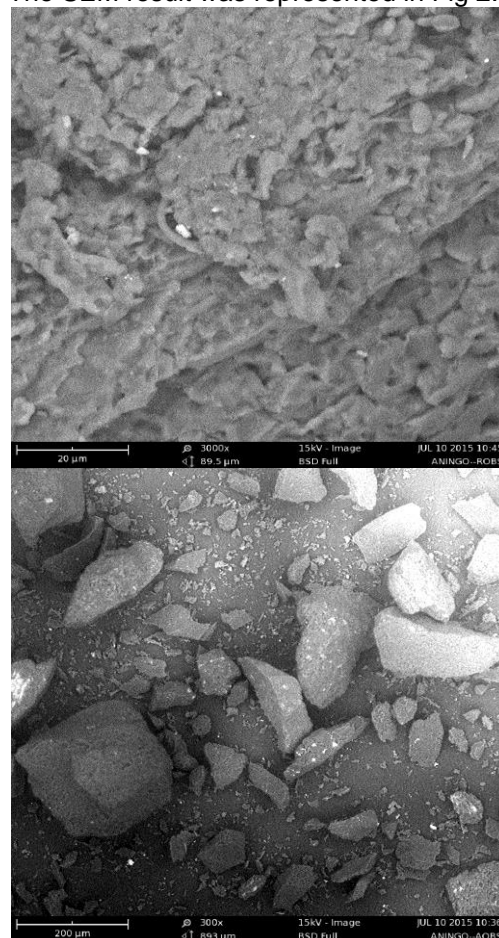
**Fig 1: Fourier Transform Infrared (FTIR) Spectra for the activated oil bean seed shell (AOBS).**

The FTIR spectra of activated oil bean seed shell carbon was determined to identify the surface functional groups responsible for binding Cd(II) ion and this was shown in fig 1 above. The activated oil bean seed shell carbon showed adsorption at 3848.65 – 3420.89cm<sup>-1</sup>, corresponding to –OH stretching vibration of hydroxyl group. Adsorption band of 2923.13 – 2726.57 cm<sup>-1</sup> represent C – H stretching, ie CH<sub>3</sub> – O group cellulose. And the band at 2359.97 represent CH<sub>3</sub> group. Adsorption band at 1733.65 – 1662.37 cm<sup>-1</sup> represent the –OH bending vibration and can also be assigned to the symmetric -COO- stretching vibrations. The adsorption band between 1457.05 – 1339.36cm<sup>-1</sup>

represent the C=C of the alkenes. The band at 1032.97cm<sup>-1</sup> represent C – O stretching vibration in cellulose, hemicelluloses and primary alcohol. The adsorption band of 721.55 and 668.48cm<sup>-1</sup> represent C-H of alkanes while band of 418.48cm<sup>-1</sup> represent the –OH out of plane bending. The FTIR spectra showed that hydroxyl, methoxyl, carboxyl, alkyl and aluminol groups are the major sites for the binding of the positively charged ion onto activated oil bean seed shell carbon.

#### SEM Analysis on ROBS and AOBS

SEM Analysis was carried out on raw oil bean seed shell and the activated carbon produced from the shell to analyse the surface morphology of the adsorbent. The SEM result was represented in Fig 2.



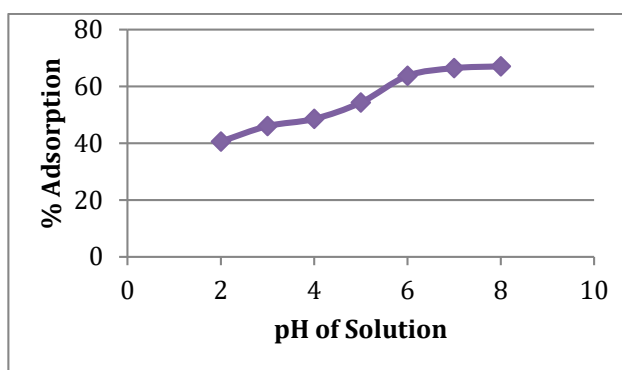
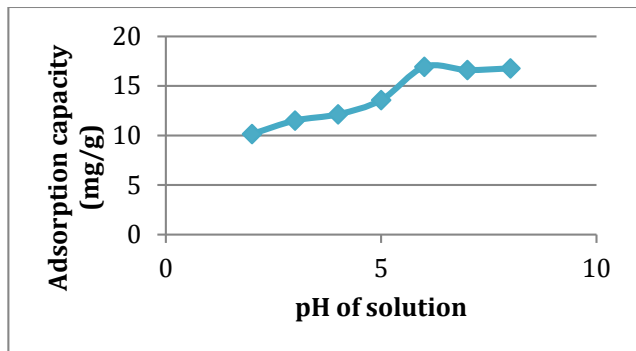
**Fig 2: SEM Analysis images on AOBS and ROBS**

It can be observed that the adsorbent (AOBS) is porous. The porous nature of oil bean seed shell activated carbon indicate enhanced sorption potential for metal ions, such that physical adsorption would play a major role in the adsorption process.

#### Effect of pH of solution

The Initial pH of solution is one of the most important parameters in the adsorption process since metal ion removal usually increase with increased pH. The pH of solution has significant impact on the uptake of heavy metal ions since it determines the surface charge of the adsorbent and the degree of ionization and specification of the adsorbate (Omar et al, 2011). The

effect of pH of ion on the adsorption of cadmium (ii) ion using activated carbon produced from oil bean seed shell are shown in fig 3:

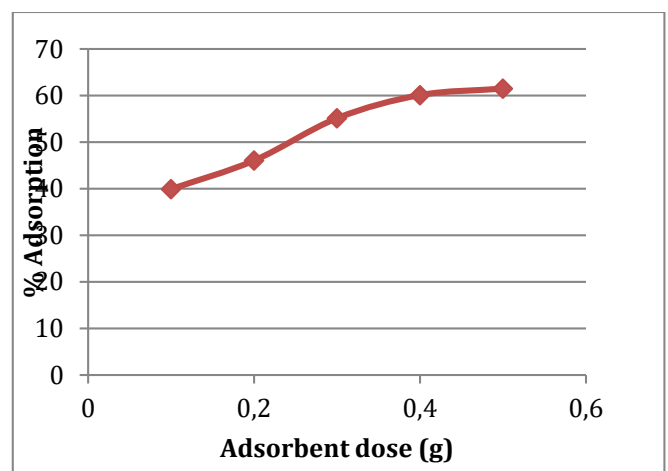
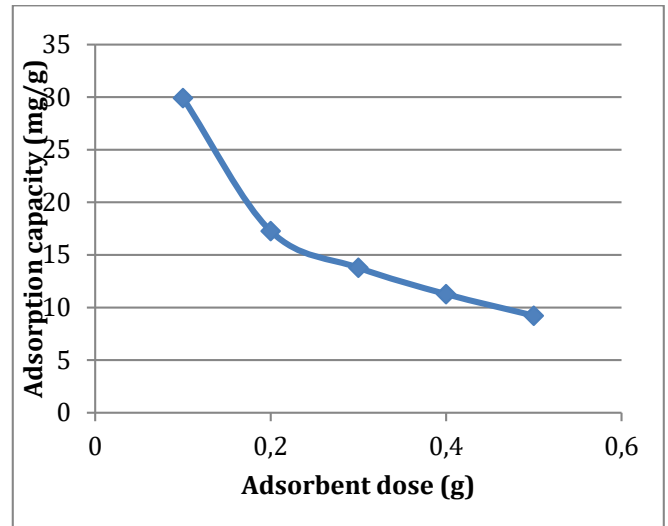


**Fig 3 : Effect of pH of solution on the adsorption of Cd (II) ion using activated oil bean seed shell carbon (AOBS)( Initial metal concentration 250mg/l, Time 60mins, Temp. 298k, Adsorbent dose 0.3g, particle size 250µm )**

It can be observed that there was a sharp increase in the adsorption of Cd (ii) using activated oil bean seed shell carbon, when the pH value of solution changed from 2.0 to 6.0 after which it started being stable at pH of 7.0 and 8.0. An optimum pH of 7.0 was selected and used for all the experiment in order to avoid the formation of metal hydroxide precipitate at higher pH. The low adsorption of the metal at low pH value is due to the fact that at lower pH more protons (H<sup>+</sup>) are present in solution and competes with the metals for active sites on the adsorbent. As the pH increases, the number of hydrogen ions in solution decreases thereby reducing the competition with the metals for the active sites of the adsorbent (Dawodu et al, 2012). This makes more sites to be available for the metal ions to bind leading to a higher adsorption with increase in pH value.

#### Effect of Adsorbent Dose

Adsorbent dose is a very important parameter for the determination of adsorption capacity of the adsorbent for the adsorbate. The effect of adsorbent dose on percentage adsorption and adsorption capacity of the cadmium (ii) ion using activated carbon produced from oil bean seed shell are presented in fig 4.



**Fig 4: Effect of adsorbent dose on the adsorption of Cd (II) ion using activated oil bean seed shell (AOBS) (Initial metal concentration 250mg/l, pH 7.0, Time 60mins, Temp. 298k, Particle size 250µm)**

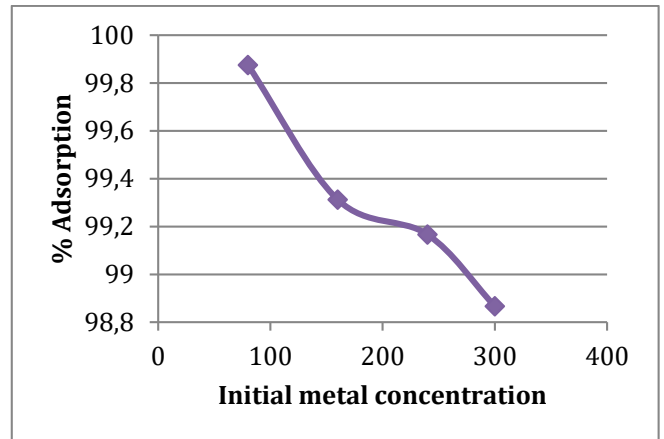
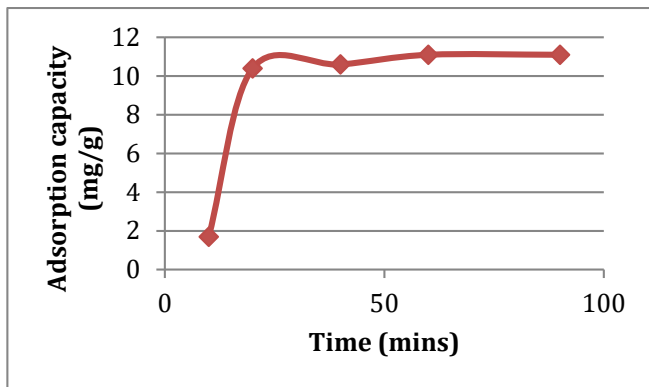
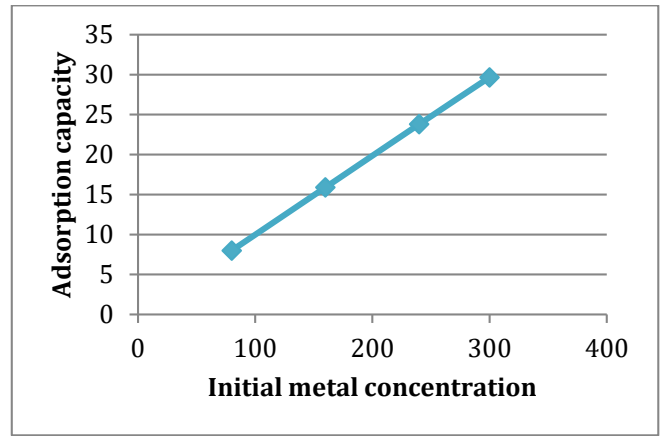
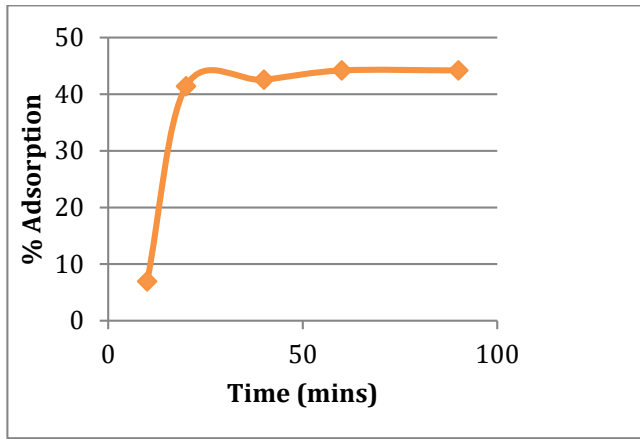
It was observed that as the mass of the adsorbent was increased from 0.1g to 0.5g, there was corresponding increase in the percentage adsorption of Cd (ii) ion from 39.9% to 61.48% while there was a decrease in the equilibrium adsorption capacity from 29.91mg/g to 9.22mg/g.

The increase in the percentage adsorption is mainly due to an increase in surface area availability of more active binding sites on the surface of the adsorbent with increase in adsorbent dose (Barka et al, 2013).

The decrease in adsorption capacity as the adsorbent dose increases is due to the decrease in the total adsorption surface area available to cadmium ion resulting from overlapping or aggregation of adsorption sites (Crini et al, 2007; Akar et al, 2009).

#### Effect of Contact time

The amount of metal ion adsorbed is a function of the time of agitation making it an important factor for effective adsorption. The effect of time on the adsorption of cadmium ion is presented in figure 5.



**Fig 5 : Effect of contact time on the adsorption of Cd (ii) ion using activated oil bean seed shell carbon.(Initial metal concentration 250mg/l, pH 7.0, Adsorbent dose 0.3g, Temp 300k, Particle size 250µm)**

It was observed that the adsorption capacity of oil bean seed shell activated carbon onto the removal of cd (ii) increases with increase in time of agitation. It was observed that the rate of adsorption of the cd(ii) was initially rapid and reduced gradually until an equilibrium time was attained. The fast adsorption at the initial stage is due to the vacant and abundant sites on the adsorbent which became used up with time and became saturated thereby attaining equilibrium (Grupta et al, 2003). Equilibrium was established around 30mins at 11.1mg/g. At the agitation time of 30mins, 44.2% of metal ion was adsorbed, after which there was no significant further adsorption.

#### Effect of Initial metal concentration

The effect of initial metal concentration on the adsorption of Cd (ii) using activated oil bean seed shell carbon is presented in fig 6.

**Fig 6: Effect of Initial metal ion concentration on the adsorption of Cd (ii) ion using oil bean seed shell activated carbon (Time 60mins, Temp 298k, pH 7.0, Adsorbent dose 0.3g, Particle size 250µm)**

It was observed that the adsorption capacities of the adsorbent increases with increase in initial metal concentration while percentage adsorption decreases with increase in initial metal concentration. At an initial concentration of 80mg/l, 7.99mg/g of the metal ion was adsorbed while at 300mg/l, 29.66mg/g metal ion was adsorbed. The percentage adsorption was 99.88% at 80mg/l metal concentration but decreased to 98.67% at 300mg/l. The increase in adsorption capacity with metal concentration is attributed to a higher concentration gradient which acts as a driving force to overcome resistances to mass transfer between the adsorbate and adsorbents (Liang et al, 2010).

The decrease in percentage adsorption with an increase in metal concentration is because at lower concentration the active sites can be occupied by metal ions, but when the metal concentration increases the active sites become saturated causing less removal of the metal ions (Meitei and Prasad, 2013).

#### Adsorption Isotherm

Adsorption isotherms are used to express the relationship between the amount of adsorbate removed from the liquid phase by unit mass of the adsorbent at a constant temperature. The isotherm parameters often give useful information on sorption mechanism, surface

properties and affinity of the adsorbent. The table below shows the adsorption isotherm parameters:

**Table 2: Adsorption isotherm parameters**

ISOTHERM MODELS	Cd (ii)
<b>Langmuir model</b>	
qL (mg/g)	34.4483
KL (L/mg)	1.383
R <sup>2</sup>	0.92
<b>Freundlich model</b>	
KF (mg/g)(mg/L) <sup>1/n</sup>	17.742
n	2.73
R <sup>2</sup>	0.970
<b>Tempkin model</b>	
B (mg/g)	5.712
A (L/g)	31.7418
R <sup>2</sup>	0.89
<b>Dubinin- Radushkevich model</b>	
qm(mg/g)	23.359
β(mol <sup>2</sup> /kJ <sup>2</sup> )	2 X 10 <sup>-8</sup>
R <sup>2</sup>	0.838

In this study Langmuir, Freundlich, Tempkin, and Dubinin – Radushkevich isotherm models were applied to the adsorption of cadmium (ii) ion on oil bean seed shell activated carbon.

### The Langmuir Isotherm

From table 2, the correlation coefficient (R<sup>2</sup>) of Cd (ii) is 0.92 which indicates a good fit of the monolayer Langmuir to the adsorption of the metal ions onto oil bean seed shell activated carbon. Also the maximum monolayer adsorption capacity qL (mg/g) for pb (II) is 34.4483. The value of the separation factor (RL) provides important information about the nature of the adsorption process. The adsorption is said to be irreversible (RL = 0), favourable (0<RL<1), linear (RL =1) or unfavourable (RL>1). For the initial concentration ranging from 80mg/l to 300mg/l, the RL values range from 0.0000968 – 0.000363 indicating a favourable adsorption of Cd (ii) onto activated oil bean seed shell carbon.

### The Freundlich isotherm model

The Freundlich isotherm model assumes a multilayer adsorption onto a heterogeneous adsorbent surface, where the sorption energy distribution decreases exponentially. From the above table, the correlation coefficient (R<sup>2</sup>) of the Cd (ii) adsorption is 0.970, indicating a good fit of the Freundlich multilayer heterogeneous adsorption model to the adsorption of Cd(ii) using the adsorbent. If the value of n lie between 1 and 10, it indicates a favourable adsorption (Das and Mondal,2011). The values of n obtained for the Cd (ii) adsorption using the oil bean seed shell activated carbon is 2.73, indicating a favourable adsorption. The adsorption capacity constant KF (mg/g)(mg/l)<sup>1/n</sup> for metal ion adsorption is 17.742.

### The Tempkin Isotherm Model

The interaction of different adsorbates on the adsorbent was not considered in the Langmuir and Freundlich isotherms. Tempkin considered the effect of the adsorbate interaction on adsorption and proposed the model.

From the above table, the correlation coefficient of the Cd(ii) adsorption is 0.89 which is lower than that of the Langmuir and Freundlich. This shows that the adsorption of Cd (ii) ion onto oil bean seed shell activated carbon does not fit well to the model as much as the two models above. The value of equilibrium binding constant A (L/g) is 31.7418 and the isotherm constant B (mg/g) which is related to heat of adsorption is 5.712.

### Dubinin – Radushkevich Isotherm

The correlation coefficient for the Cd (ii) adsorption is given as R<sup>2</sup> = 0.838 in the above table which shows that the model does not fit as much as the first two models above. Also, the constants qm and β were calculated from the intercept and slope of the plot of ln qe versus ε<sup>2</sup>. The values of qm and β are given as 23.359 and 2 X 10<sup>-8</sup> respectively.

**Table 3: Kinetic parameters for the adsorption of Cadmium (ii) on oil bean seed shell activated carbon.**

Kinetic model	Cd (II)
qe <sub>exp</sub> (mg/g)	11.1
<b>Pseudo – first – order</b>	
qe <sub>cal</sub> (mg/g)	2.535
K <sub>1</sub> (min <sup>-1</sup> )	0.01383
R <sup>2</sup>	0.191
<b>Pseudo – Second – Order</b>	
h (mg/g min)	0.3447
K <sub>2</sub> (g/ mg min)	7.942 X 10 <sup>-3</sup>
qe <sub>cal</sub> (mg/g)	20.833
R <sup>2</sup>	0.442

The kinetic parameters for the adsorption of cadmium (ii) ion on the oil bean seed shell activated carbon was fitted to the Pseudo- first – order and Pseudo – second – order models. The two models did not provide a good fit to the experimental data for the adsorption of the metal ion. This can be seen from their R<sup>2</sup> values which are 0.191 and 0.442 for the first order and second order respectively. The initial sorption rate (h) is 0.3447mg/gmin.

Nevertheless, the calculated qe value of the Pseudo – first – order and Pseudo – second – order differed widely with the experimental qe value.

**Table 4: Adsorption thermodynamic parameters**

Meta I ions	Tem p (k)	Kc	ΔG <sup>o</sup> (kJ/mol)	ΔH <sup>o</sup> (kJ/mol)	ΔS <sup>o</sup> (j/molk)
Cd(ii)	303	0	0		
	313	1.2727	-627.410	13610	45.253
	323	1.5536	-1183.197		
	333	1.6096	- 1317.84		

From table 4, it can be observed that ΔG<sup>o</sup> values at all temperatures for the metal ion used are all negative. This indicates that the adsorption is spontaneous in



nature. The value of  $\Delta H^0$  obtained for the metal ion is positive, indicating an endothermic nature of the adsorption process, which explains the fact that adsorption efficiency increased with increase in temperature (Akpomie and Dawodu, 2014). The positive value of  $\Delta S^0$  indicates an increase in randomness at the solid-solution interface during the adsorption process.

## CONCLUSION

In this study, activated carbon produced from oil bean seed shell was used as a low cost adsorbent for the removal of Cd (ii) from aqueous solution. The characterization results show that high surface area, bulk density, pH, low ash content, low moisture content, high fixed carbon, low volatile matter must have contributed to the high adsorption capacity of the adsorbent used. The FTIR spectra showed that certain functional groups, hydroxyl group, methyl group etc, were responsible for binding the metal ions from solution. SEM analysis indicated an increase in the porosity of the activated oil bean seed shell carbon as compared to the raw sample. The adsorption isotherm can satisfactorily be described by both the Langmuir and Freundlich models. The maximum monolayer adsorption capacity of Cd(ii) ions onto oil bean seed shell activated carbon was gotten to be 34.4483mg/g. The adsorption kinetic parameters did not fit the pseudo-first-order and pseudo-second-order model. There is a wide discrepancy between the calculated  $q_e$  values and the experimental  $q_e$  value. The positive value of  $\Delta H^0$  indicates an endothermic adsorption process. The results of this work indicate that the adsorbent used is a good low-cost adsorbent for the adsorption of cadmium ion.

## REFERENCES

- [1] S.T. Akar, et al, Biosorption of reactive textile dye from aqueous solutions utilizing an agro – waste. *Desalination*, 2009, 249 (2); 757 – 761.
- [2] K.G. Akpomie, and F.A. Dawodu, Efficient abstraction of nickel (ii) and magnesium (ii) from solution into an alkaline modified montmorillonite. *Journal of Taibah University Science*, 2014, 8(4): 134 – 147.
- [3] E. Augustine, Ofomaja, Kinetic and Pseudo isotherm studies of 4- nitrophenol adsorption onto *Mansonia* wood sawdust, *Industrial crops and product*, 2011, 33, 418 – 428.
- [4] E. Ayransi, and O. Duman, Adsorption behaviours of some phenolic compounds onto high specific area activated carbon cloth, *J. Hazard Mater*, 2005, 124 – 132.
- [5] N. Barka, M. Abdennouri, M.E. Makhfouk, S. Qourzal, Biosorption characteristics of cadmium and lead onto eco-friendly dried cactus cladodes, *J. Environ. Chem. Eng*.1: 2013, 144- 149.
- [6] K.G. Bhattacharyya, and S.S. Gupta, Kaolinite, montmorillonite and their modified derivatives as adsorbents for removal of Cu (ii) from aqueous solution to the montmorillonite/ water interface, *colloid surf. A* 166, 2000, 153 – 159.
- [7] S. Chand, V.K. Aggarwal, P. Kumar, Removal of hexavalent chromium from the wastewater by adsorption, *Indian J. Environ. Health*, 1994, 36 (3) 151- 158.
- [8] G. Crini, et al, Removal of C. I .Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin – based adsorbent: Kinetic and equilibrium studies. *Sep. Purif. Technol*, 2007, 53(1): 97-110.
- [9] B. Das, and N.K. Mondal, Calcareous soil as a new adsorbent to remove lead from aqueous solution: equilibrium kinetic and thermodynamics study. *Universal Journal of Environmental Research and Technology*, 2011, 1 (4) : 515 – 530.
- [10] F.A. Dawodu, and K.G. Akpomie, Simultaneous adsorption of Ni (ii) and Mn (ii) ions from aqueous solution unto a Nigerian Kaolinite clay.2014.
- [11] F.A. Dawodu, G.K. Akpomie, I.C. Ogbu, Application of kinetics rate equations on the removal of copper (ii) ions by adsorption unto aloji kaolinite clay mineral. *Int. J. Multidisc. Sci. Eng*.2012, 3, 21 – 26.
- [12] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Sorption and structure of active carbons adsorption of organic vapors, *J .Physichem*. 1947, 21 1351 – 1362.
- [13] O.A. Ekpete, and M. Horsfall, JNR, Preparation and characterization of activated carbon derived from fluted pumpkin stem waste ( *Telfaira Occidentalis* Hook F) *Res. J. Chem. Sci. Vol* 1(3). 2012.
- [14] K.Y. Foo, and B.H. Hameed, Microwave assisted regeneration of activated carbon. *Bioreservoir Technology*.2012, 11a, 234 – 240
- [15] C. Gimba, and I. Musa, Preparation of activated carbon from agricultural waste : cyanide binding with activated carbon matrix from coconut shell. *J. Chem. Nigeria* 2007, 32, 167- 170.
- [16] M. Igbal, A. Saeed, S.I. Zafar, Hybrid biosorption : an innovative matrix to enhance the biosorption of Cd (ii) from aqueous solution. *J. Hazard. Mater*. 2007, 148, 47 – 55.
- [17] S., Liang, X. Guo, N. Feng, and Q. Tian, Isotherm, Kinetics and thermodynamics studies of adsorption of Cu (ii) from aqueous solution by Mg<sup>2+</sup> / K<sup>+</sup> type orange peel adsorbents. *Journal of Hazardous Material* 2010, 174: 756 – 762.
- [18] M.D. Meitei, and M.N.V. Prasad, Lead (ii) and cadmium (ii) biosorption on *spirodela polyrhiza* (L) Schleiden biomass. *Journal of Environmental Chemical Engineering*, 2013, 1: 200 – 207.
- [19] E. Omar Abel Salam, A. Neama Reiad, M. Maha Elshafei. A study of the removal characteristics of heavy metals from wastewater by low cost adsorbents. *Cairo university Journal of Advanced Research*, 2011, 2, 297 – 303.
- [20] D.O. Onwu., *Coal fundamentals, conversion and processing Technology*, Immaculate Publications, Enugu. 1999.