# Crude Oil Sorption onto Groundnut Shell Activated Carbon: Kinetic and Isotherm Studies

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**Abstract:** An adsorbent of Activated Groundnut Shell Carbon (AGSC) was prepared to adsorb crude oil from water solution. The study of its adsorption mechanism was studied in terms of equilibriumand kinetics.Popular Freundlich, Langumiur, Temkin and Dubinin Radushkrvich models were adopted to study the isotherms. Although Dubinin Radushkrvich model ($R^2 = 0.368$) is not in agreement with the equilibrium data but Freundlich ($R^2 = 0.992$), Langumiur ($R^2 = 0.985$) and Temkin ($R^2 = 0.54$) models were observed to follow the data with Freundlich model best described the data ($R^2 = 0.992$). The data were also subjected to kinetic studies using largergreen first order, pseudo second order and intra-diffusion kinetic models. It was found that pseudo-second order with the degree of fitness of $R^2 = 0.99, 0.93, 0.99, 0.97$ and $0.99$ for crude oil samples A,B,C,D and E respectively, fitted the data better than Largergreen which has the degree of fitness as $R^2 = 0.89, 0.65, 0.66, 0.66$ and $0.68$, respectively for A, B, C, D and E. The results from the intra-diffusion model revealed that the intra-diffusion and external mass transfer are both rate determining stages of the adsorption process. The results of the study implies that AGSC is a good mop-up and low-cost alternative medium for oil spilled surfaces.

**Key words:** Adsorption, carbon, equilibrium, groundnut-shell, kinetic, models

## INTRODUCTION

Over the years, crude oil spill and its concomitant pollution have been in a front burner in environmental issues over the world and in particular the oil rich Niger-delta of Nigeria. Its attendant pollution upsets the ecological balance of the oil spilled area. In the case of spill on land, crude oil alters the physiochemical properties of the soil (Gesinde *et al.*, 2008). Ogaji *et al.* (2005) further reported that soils soaked with crude oil instantly loses fertility and initiates environmental degradation. Also, oil spill results in the changes of soil pH which influences the solubility and abundance of micro-nutrients (Broder and Zeller, 2010). Johnson *et al.* (1974) observed glaring imbalance of carbon- nitrogen ratio in an oil-soaked soils. Furthermore, large concentration of crude oil on the soil surface depletes and slows down oxygen diffusion in the lower horizons limiting robust agricultural usage of the soil (Molnaa and Grubbs, 1989). In aquatic environment; different aquatic species have varying sensitivity to crude oil pollution in water. However, the crude oil spill in an aquatic environment floats and block out sunlight initiating the death of Phytoplankton and seaweed, sources of food and indeed the chief sources of food chains, hence starving life under the spill (Gwendoline, 2010). In most cases, fishes swim away from the spill into the deeper water reducing their likelihood of been affected and the surviving ones, growing stunted (Nilsson, 1971). Johnson *et al.* (2000) observed that fishes whose growths are retarded by aggressive environment occasioned by crude oil spill pose serious health problems to consumers. On larger mammals in water, oil has also been known to cover the blow holes of whales, causing death. It attaches to the fur of otters and other animals with fur or feathers. It soaks the feathers and cause these animals to freeze because their protective coat has been destroyed (Gwendoline, 2010). Crude oil has become one of the most frequently detected underground water pollutants caused by leakages from underground storage tanks, Pipelines and other components of crude oil distribution systems (Kharoune *et al.*, 2001). In view of the aforementioned, there has been a growing concern regarding the treatment of water and wastewater in recent years. Generally, the conventional method of water and wastewater treatment technologies including flocculation, ultrafiltration, biological treatment and coagulation (Suidan *et al.*, 2005; Ayotamuno *et al.*, 2006,

Yang-Guipeng *et al*., 2006; Nilsson, 1971) do not seem to be economically viable. Specifically, several treatment measures have been applied to contain with the degraded crude oil-polluted water. Given its high aqueous insolubility, the use of chemical dispersant in addition to being less effective and expensive, introduces more pollutant in the system (Ayotamuno *et al*., 2006, Odokuma *et al*., 2003,). The high running cost of photochemical degradation of crude oil has hampered its general application although it is quite effective in removing spilled crude oil in water (Choy *et al*., 1999). Sorption technologies including adsorption are simpler and more robust in addressing water and wastewater issues although conventional porous materials such as fly ash, clay, activated carbons and silica materials have been reported to have non-uniform pore structure and low adsorption capacities with slow adsorption kinetics (Goswami and Gosh, 2005) as their qualities run counter to that of ideal adsorbent with assessable inter-linked pore structure, uniform pore size distribution, high surface area and physical/chemical stability (Kim *et al*., 2003; Rengaraj *et al*., 2004). Groundnut shell is an agricultural based waste material and this material has the potential to sequester metals from solutions (Malik *et al*., 2006). The activated carbon prepared from groundnut shell has been utilized for the sorption of dyes methylene blue (Kannan and Sundaram, 2001) and malachite green (Malik *et al*., 2007). Several other researcher have successively remove crude oil from a contaminated water using ordinary meshed groundnut shell due to its well developed pore structure and large surface area (Anne *et al*., 2009) but the activated meshed groundnut shell and full investigation of kinetic and mechanism of activated groundnut shell in removing crude oil from contaminated water has not been reported.

Therefore the objective of this study was to assess the adsorption capacity and mechanisms of the meshed activated ground nut shell in the adsorption of crude oil. Use of Langmuir, Freundlich, Timkin isotherm models were made to evaluate the sorption capacity of the adsorbent. The sorption dynamics were analyzed using pseudo-first order, pseudo second order, and Dubinin Radushkrvich and intraparticle kinetic models.

## MATERIALS AND METHODS

2000g of groundnut shell collected from the groundnut oil extraction mill at Kaduna Northern Nigeria, was washed and pyrolyzed at temperature of between 300-400ºC for 2 h and 30 min. The pyrolysed groundnut shell was carefully meshed into powder and sieved using sieve of 1.18 mm to get particles of uniform size. 200 g of the well sieved pyrolysed material was transferred into a beaker containing 150 mL of 0.1 m hydrochloric acid and mixed until the mixture formed a paste. The paste was then transferred into a dry crucible and oven dried for 1 h at 150ºC before it was heating in muffle furnace at 800ºC for 2 h to increase its surface area. After which, it was washed with a distilled water to bring its pH range to 7 and oven dried for 3 h to get an activated groundnut shell based carbon (AGSC) (Palte 1).

**Characterization of the adsorbent:** Ph of the activated adsorbent (AGSC) was determined by dissolving 2.5 g of the activated adsorbent into 50 mL of distilled water, the mixture was heated and stirred adequately for some minutes to ensure proper dilution of the sample. The mixture was filtered and the pH of the clear solution was read using digital pH meter. The particle size of the adsorbent was determined by adopting ASTM D2862. Bulk density, moisture content, ash content, pore volume and porosity were determined using the methods adopted by suidan *et al*. (2005).

**Characterization of the adsorbate:** Five crude oil samples denoted as samples A, B, C, D and E were used as adsorbates. The crude oil samples were collected from five different oil wells in Niger-delta, south-south region of Nigeria. Their Total Hydrocarbon Concentrations (THC), density, specific gravity, viscosity and refractive index were analyzed using standard methods.

**Adsorption isotherm study:** Batch experiment was adopted for the isotherm study. Crude oil samples of five different initial concentrations were put in five sealed bottles containing fixed amount of the activated groundnut shell (1 g/L) (each bottle for one sample). The bottles were agitated by a rotary shaker at 180 rpm for five days to attain equilibrium. Each experiment was carried in three replicates. After the agitation, samples were withdrawn at fixed intervals of 10 min for 70 min and centrifuged. Supernatants of the centrifuged samples were analyzed for THC and the equilibrium capacity of the activated groundnut shell was determined using this relationship (Chen *et al*., 2010).

$$q_e = \frac{(C_e - C_o)C}{M} \qquad (1)$$

**Effects of initial concentration:** Adsorption kinetics was further investigated by studying the effects of the initial concentrations of the adsorbate. In this regards, the same amount of activated groundnut shell (1 g/L) as used in the isotherm study was added to 250 mL bottles each containing the initial concentrations of each crude oil sample. The solution was stirred and agitated by a rotary shaker moving at 180 rpm for a period of five days. Supernatants of the agitated and centrifuged solution were withdrawn at predetermined periods and analyzed for

Plate 1a: images of the groundnut shell and its activated form

THC. Each experiment was done in triplicates. The raw material collections and the experiments were carried out between October 2009 to December 2010.The laboratory work was performed in the chemistry laboratory of the Chemistry Department of Federal University of Technology Owerri Nigeria.

## RESULTS AND DISCUSSION

Characterization of the AGSC was carried out according to the method adopted by Suidan *et al*. (2005). Results obtained showed that AGSC contained the following; 0.602 g/cm$^3$, 0.224%, 0.149%, 1.044 mL, 0.201 of density, moisture content, ash content, pore volume and porosity respectively. A recommended standard method of analysis (ASTM D2862) was adopted for the determination of the mean particle sizes and the value was 29.738 μm. The results were the mean values of the three replicated experiments. Observations of Malik *et al*. (2007), Aminu *et al*. (2010) and Itodo (2011) have close resemblance with the present work but vary appreciably on the level of moisture content. This could be attributed to differences in the drying temperature value during the activation process of the adsorbent. Total Hydrocarbon Concentrations (THC) of the five crude oil samples before the adsorption process were analyzed to be as follows; sample A= 6045 ppm, sample B= 4393 ppm, sample C = 8508 ppm, sample D = 11593 and sample E = 5220 ppm. From the results, sample D has the highest THC values followed by sample C with the least value ascribed to sample B.

**Adsorption isotherm:** The isotherm studies which focused on the relationships between the mass of the adsorbate per unit weight of adsorbent and liquid phase equilibrium concentration of the crude oil have their results analyzed by the well-known isotherm models; freunlinch, langumir and temkin adsorption isotherms. Freundlich adsorption isotherm model is mostly adopted to describe the adsorption of inorganic and organic components in solution (Chang *et al.*, 2003). This model explains the uptake of adsorbate to take place on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely as the concentration increases (Itodo, 2011). Freunlich adsorption model is expressed as:

$$q_e = K_f C^{\frac{1}{m}} \qquad (2)$$

Equation (2) was linearized to get:

$$\ln q_e = \ln K_f + \frac{1}{m}\ln C_e \qquad (3)$$

Table 1: Pseudo-first, second order and intra-diffusion parameters for sorption of crude oil onto AGSC

| Name of adsorbate | Conc. of hydrocarbons (mg/L) | Pseudo-first-order $K_1$ rate constant ($h^{-1}$) | $R^2_1$ | Pseudo-second $K_2$ order rate constant($h^{-1}$) | $R_2^2$ | Intradifusion constants Kp (mg/g) ($h^{1/2}$) |
|---|---|---|---|---|---|---|
| Crude oil A | 6045 | 2.10 | 0.89 | 0.189 | 0.99 | 62.59 |
| B | 4396 | 2.48 | 0.65 | 0.27 | 0.93 | 47.78 |
| C | 8508 | 2.42 | 0.66 | 0.098 | 0.99 | 105.6 |
| D | 11593 | 2.40 | 0.66 | 0.008 | 0.97 | 145.7 |
| E | 5220 | 2.46 | 0.69 | 0.14 | 0.99 | 75.59 |

Table 2: isotherm models and constants for the sorption of crude oil On the AGSC

| Isotherm Models | Isotherm constants | | |
|---|---|---|---|
| Dubinin Radushkrvich | E | $q_s$(mg/g) | $R^2$ |
| $ln(q_e)=lnq_s-B\varepsilon^2$ | 0.891 | 0.702 | 0.368 |
| Temkin | B | A | $R^2$ |
| $q_e=BlnA+BlnC_e$ | 784.8 | 5508 | 0.54 |
| Freunlich | $K_F$ | m | $R^2$ |
| $\ln q_e = \ln K_f + \dfrac{1}{m}\ln C_e$ | 5.75 | 1.56 | 0.992 |
| Langumuir | $q_m$ | $K_L$ | $R^2$ |
| $q_e = \dfrac{q_m K_L C_e}{1+ K_L C_e}$ | 0.76 | 1.14 | 0.985 |

$K_f$ and $m$ is the intercept and the gradient of the plot of $\ln q_e$ against $\ln C_e$ respectively. The plot as presented in Fig. 1 shows that adsorption follows the freudlich isotherm model and better fits the model more than the other models.

Appreciably high correlation coefficient, $(R^2)$ value of 0.992 attests to that claim. Also, the value of m (1.56) which falls within the limit 0f 1-10 as reported by Selvaraj *et al*. (2007) gave credence to the claim that AGSC has good adsorption capacity for the crude oil (Table 1). The fitness of freundlich adsorption isothermal model in this study is in line with that of Malik *et al*. (2007) where Adsorption of malachite green dye on groundnut shell waste based powdered activated carbon was carried out. The values of m and $K_f$ which were calculated from gradient and intercept, respectively are also shown in Table 1. This observation which is in line with that earlier made by Itodo (2011) that the amount of adsorbate adsorbed increased infinitely as the concentration increased was further substantiated in this study in a plot to show the adsorption pattern of crude oil at different initial concentrations onto the AGSC. Figure 1 shows the level of adsorption of crude oil at various initial concentrations in a plot of the relationship between the amounts of adsorbed crude oil with time. It was observed that the highest amount of crude oil adsorbed onto the AGSC was that with initial concentration of 11593 mg/L. Since freudlich model best fitted the crude oil adsorption process on the AGSC, it implied that the AGSC has heterogeneous surface and the uptake of the adsorbate(crude oil) took place on a by multilayer adsorption process (Chang *et al.*, 2003).

Kim *et al*. (2004) stated that the langumuir adsorption isothermal model assumes that the uptake of adsorbates is better performed on a homogenous surface of monolayer adsorption. The model also assumes that energies of adsorption of the adsorbates to the surface is uniform as the adsorbing materials are free from interaction with the already adsorbed materials (Monika *et al*., 2009).

The Langmuir adsorption isotherm model is presented as:

$$q_e = \frac{q_m K_L C_e}{1+ K_L C_e}$$

Taking the inverse of the equation and expanding the variables transforms the equation to:

$$\frac{1}{q_e} = \frac{1+ K_L C_e}{q_m K_L C_e} = \frac{1}{q_m K_L C_e} + \frac{K_L C_e}{q_m K_L C_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$$

Values of $q_m$ and $K_L$ were determined by evaluating the gradient and intercept of the plot of $1/q_e$ against $1/C_e$.

The linear plot of $1/q_e$ against $1/C_e$ as shown in Fig. 2 produced a linear curve with coefficient of correlation $R^2$, $q_m$ and the $K_L$ values shown on Table 2.

The coefficient of correlation value $(R^2)$ shows a high correlation value of 0.985 indicating reasonably good correlation though langumir isotherm did not fit the experimental data better than freudlich isotherm.

Temkin adsorption isotherm studied the effects of the indirect interactions of the adsorbate molecules with the result that the heat of adsorption of all the molecule decreases linearly with coverage due to adsorbents interactions (Choy *et al*., 1999). Temkin adsorption model is expressed as in Eq. (4).
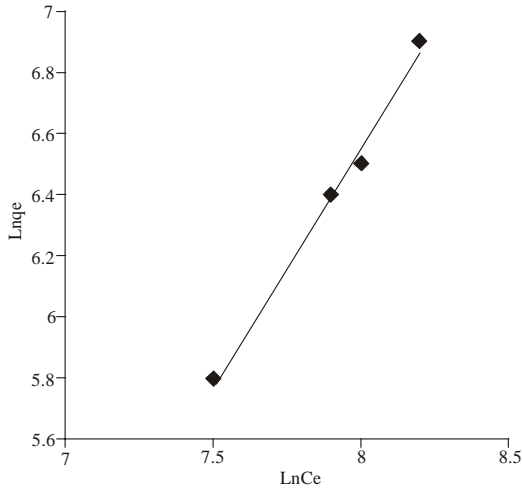
Fig. 1: Represents freundlich isotherm model plot on the adsoprtion of crude oil onto the AGSC
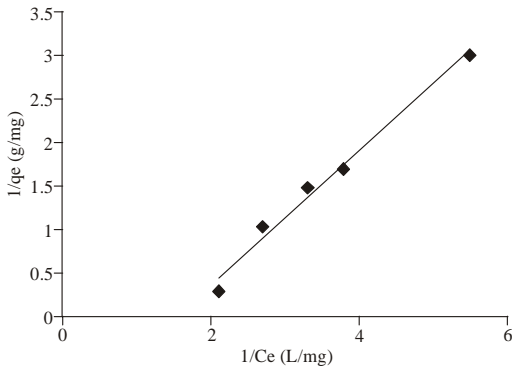


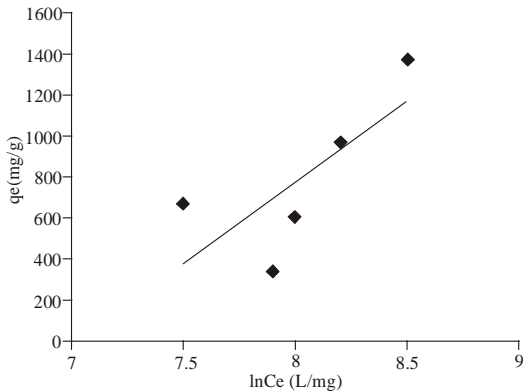Fig. 2: Represents the langumiur model plot on the adsorption of crude oil onto AGSC



Fig. 3: Represents temkin model plot on crude oil adsorption onto AGSC

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e \qquad (4)$$

where,

$$\frac{RT}{b} = B \qquad (5)$$

Substituting Eq. (5) in (4), gives that:

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

The sorption data were analyzed by plotting $q_e$ Vs $C_e$ as shown in Fig. 3. From the graph, constants A and B were determined by reading off the intercept and gradient of the plots respectively. The values of $R^2$, A and B are shown on Table 2. The table shows the coefficient correlation ($R^2$) of 0.56, the $R^2$ is much lower than langumir and fruedlich isotherm. Temkin adsorption isotherm has produced reasonably good fit in some experimental data in the pass. For instance the work of Itodo (2011) on the derived low cost biosorbent as water decolourizer where semi dried groundnut shell was used as adsorbent is an example.

Another model used for the analysis of the isotherm data was that proposed by Dubinin Radushkrvich and expressed as:

$$\ln(q_e) = \ln q_s - B\varepsilon^2 \qquad (7)$$

where;

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

R is the gas constant (8.31J/mol K), T is the absolute temperature.

B expresses the free energy E of sorption per adsorbate molecule as it transfers to the adsorbent surface and can be computed using the following relationships:

$$E = \frac{1}{\sqrt{2B}} \qquad (9)$$

Values of B and E were deduced through the determination of gradient and intercepts respectively of $\ln q_e$ Vs $\varepsilon^2$ plot. From the plot and value of the correlation coefficient, $R^2$ (0.368) Dubinin Radushkryich model presented poorer fit of the experimental data than the other isotherns. The values are shown in the Table 2.

**Sorption mechanism:** The rate of solute uptake of adsorbate onto an adsorbent characterizes the efficiency of sorption. In this regard, the kinetic of adsorption of crude oil onto an activated groundnut shell was first studied in this work by knowing the effects or sorption efficiency of different initial concentrations of the adsorbate as displayed in Fig. 4.

The figure shows a gradual increase in crude oil uptake (q) of all the initial concentrations with time up to the highest level (plateau) before it showed a decrease and
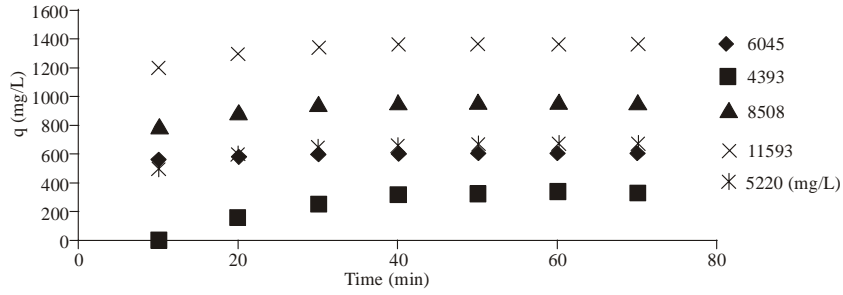
Fig. 4: Adsorption pattern of crude oil onto the activated groundnut oil shell various initial concentrations
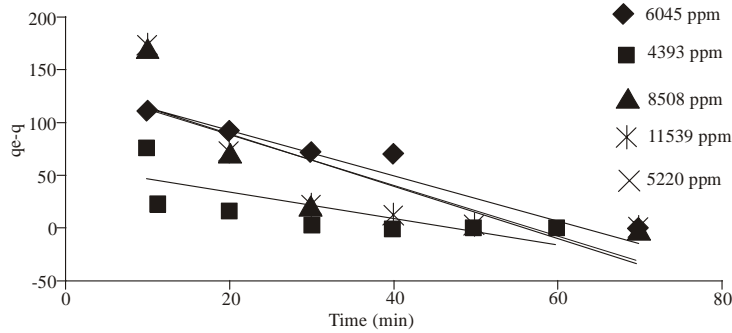


Fig. 5: Lager green plots for various initial concentrations of crude oil
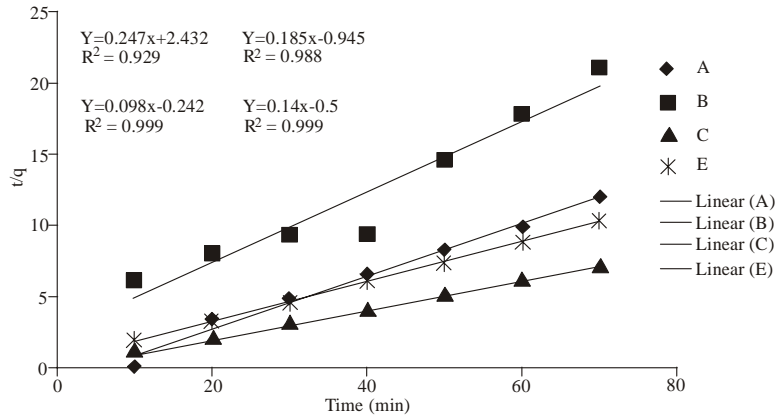


Fig. 6: Pseudo-second order plot for crude oil sorption onto AGSC

thereafter remained constant. This implies that the rate of adsorption that is, the driving force ($q_e$-q) decreased with time. It is readily understood that number of available sites on the adsorbent surface decreased as adsorption took place. This observation is consistence with that of numerous researchers who studied varieties of adsorbates/adsorbent adsorption (Chen *et al*., 2010; Selvaraj *et al*., 2007; Aminu *et al*., 2010). To further investigate the mechanism of sorption of crude oil onto the activated ground-nut shell, pseudo-first order kinetics by largegreen (Selvaraj *et al*., 2007), intra-particle diffusion process by weber and morris (Akkaya *et al*.,

2007), pseudo-second order(Ho and Mckay, 1999) and Boyd equation of 1947 were adopted and described as follows:

Pseudo first order kinetics expressed as:

$$\frac{dq}{dt} = k_{1(qe-qt)} \tag{10}$$

was integrated and boundary conditions at t = 0 to t = 1 and q = 0 to q = q inserted to give:
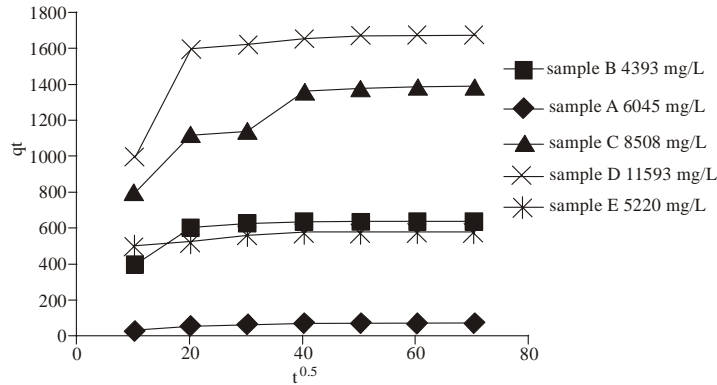
$$(ln_{qe}-q_t)=ln_{qe}+k_{1t} \tag{11}$$

Fig. 7: Intradiffusion plot of crude oil sorption onto AGSC

$K_1$ (h$^{-1}$) describes the pseudo first order adsorption rate constant, $q_e$ is the values of adsorption at equilibrium, that is, the amount of crude oil hydrocarbon adsorbed at equilibrium, while $q_t$ is the amount adsorbed with time. A linear Plot of ($lnq_e$-$q_t$) against time, t at different initial hydrocarbon concentrations helped to calculate the slopes and intercepts of the plots which were used to determine the rate constants and the equilibrium capacity $q_e$. Similarly, the pseudo-second order kinetic is expressed as:

$$\frac{dq}{dt} = K_2 (q_e - q)^2 \qquad (12)$$

Inserting the boundary conditions as stated above, the equation becomes:

$$\frac{1}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (13)$$

while $q_e$, and t remain as previously defined. $K_2$ is the pseudo-second order rate constant. $K_2$ and $q_e$ values were deduced from the straight plot of t/q vs t.

Figure 5 and 6 show the plot of largergreen and pseudo-second order kinetic model respectively for various initial concentrations of crude oil.

From the figures, the experimental data were well represented by the two models. Table 1 shows the initial concentrations of the hydrocarbons, pseudo first, second order kinetics and intra-diffusion constants and their correlation coefficients. It was observed form the table that the correlation coefficients of pseudo- first order kinetics ($R_1^2$) for various initial concentrations were within the range of between 0.65-0.89 indicating a fairly fit of the kinetic model to the data. Pseudo-second order kinetic model produced higher coefficient of correlation ($R_2^2$) of between 0.93-0.99 than the pseudo-first order kinetic model, implying that pseudo-second order kinetic

model produced a better fit to the data. It can therefore be concluded that mechanism of adsorption in this study conforms with the pseudo-second order reaction which is in line with the conclusions of Chen *et al*. (2010), Malik *et al*. (2006) and Selvaraj *et al*. (2007).

Use was also made of the intra-particle diffusion kinetic model to further study the adsorption mechanism. The kinetic model is given as:

$$q_t = K_p t^{0.5} \qquad (14)$$

According to Oladoja *et al*. (2008), Akkaya *et al*. (2007) and Selvaraj *et al*. (2007), Weber and Morris intra-particle diffusion is the rate determining factor if the plot of $q_t$ VS $t^{0.5}$ yields a straight line passing through the origin otherwise the external mass transfer determines the rate-controlling step of the adsorption process. Kp which is the intra-particle diffusion constant is determined by the slope of the plots and are shown on Table 1. It can be seen that none of the curves in the plots of $q_t$ VS $t^{0.5}$ passed through the origin as shown in Fig. 7.

This trend of relationship suggested that intra-particle diffusion is not the only rate- controlling-step. Although, one can observe from Table 1 that Kp increased with values of initial concentrations of the crude oil which was also reported by; Yang *et al*. (2003) and Chatzopoulos *et al*. (1993) to mean that intraparticle diffusion, D increases with increase initial concentrations. Chatzopoulos *et al.* (1993) strengthen this claim with the relationship in Eq. (15).

$$Kp = \frac{6qe}{R} \sqrt{\frac{D}{\pi}} \qquad (15)$$

This equation further implies that Kp increased with the initial concentrations due to increase in and Boyd equation presented by Chen (2010) further interpreted the
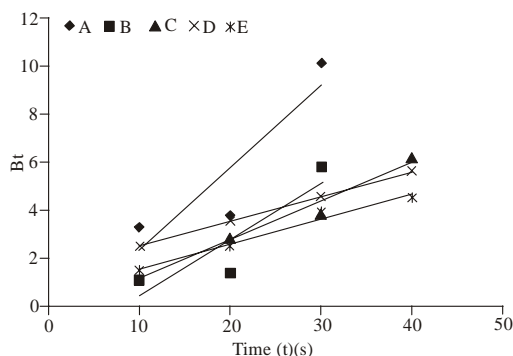
Fig. 8: Boyed plot for crude oil sorption onto AGSC

rate determining step of the diffusion. The equation is expressed as:

$$F = 1 - \frac{6}{\pi^2} e^{Bt} \qquad (16)$$

If F is set to be equal to $\dfrac{q}{q_e}$ and substituted in the equation, $B^t$ can be expressed as:

$$Bt = -0.4977 - \ln\left[1 - \frac{q}{q_e}\right] \qquad (17)$$

Kumar *et al.* (2005) stated that if the plots of the values of Bt against time(t) yield straight curves without passing through the origin, the diffusion process is said to be external-mass -transfer controlled. In this study, the curves in Fig. 8.

Did not pass through the origin signifying that the external-mass-diffusion transfer of crude oil onto AGSC is not the main rate determining step. This observation conforms with that of Kumar *et al.* (2005).

## CONCLUSION

The adsorption of crude oil onto AGSC has been studied. The equilibrium adsorption isotherm analysis using langumir, freundlich, temkin, and Dubinin Radushkrvich was carried out.. Temkin, langumuir and freundlich isotherm models fitted the equilibrium data reasonably well, whereas Dubinin Radushkrvich model produced a poor fit of the equilibrium data. Results from the freundlich isotherm model are most significant, followed by langumir and temkin with Dubinin Radushkrvich model result being the least significant. Kinetics of adsorption was equally carried out. The adsorption kinetic data were analyzed using largergreen

first-order model, pseudo second order model and intra-particle diffusion model. The adsorption of crude oil onto the AGSC was better described by the pseudo second order kinetic model. The study of adsorption mechanism also showed that both intra-diffusion and external mass transfer were parts of the rate controlling steps of the process. Adsorption techniques using AGSC medium has provided cheap alternative to the conventional methods and good waste management approach.

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