

Modelling Of The Kinetic And Equilibrium Sorption Behaviour Of Crude Oil On HDTMAB Modified Nigerian Nanoclays

Nwankwere Emeka Thompson, Gimba Casimir Emmanuel, Ndukwe Iloegbulam George, Isuwa Kari Adamu

Abstract: This study explores the feasibility of using local nanoclays as starting materials for sorbents with potential to treat crude oil polluted aquatic environment. The nanoclays have been converted into environmentally friendly and hydrophobic sorbents by a hydrothermal method under mild conditions using Hexadecyltrimethylammonium bromide (HDTMAB) as intercalant. Batch sorption studies were studied for oil concentration (0.5-5.0 g/100ml) and contact time (1-30 mins). An attempt to describe the crude oil sorptive behaviour of the organoclays by applying popular adsorption models were discussed and the experimental methods adopted for the determination and estimation of the sorption coefficients have also been described. The Langmuir, the Freundlich and the Dubinin-Radushkevich adsorption models were applied to experimental equilibrium data. Also the kinetic properties of the sorption procedure were evaluated using the pseudo-second-order, Elovich and the intraparticle diffusion of Weber and Morris kinetics models. It was discovered that the sorption process best fitted the Langmuir and the Pseudo-second-order rate models. It was concluded that the organoclays have a good affinity for the crude oil, the sorption process was mostly by monolayer coverage, the manner of sorption by chemisorption and that diffusion was not only the rate-controlling step.

Index Terms: Equilibria, HDTMA, kinetics, oil Spill, organoclays, sorption.

1 INTRODUCTION

CRUDE oil and its derivatives are one of the most important sources of energy in the world. However, when this vital resource is out of control, it can destroy lives and devastate the environment and economy of a particular region [1]. Oil spills may be due to the release of crude oil or its products from pipes, tankers, ships, offshore platforms resulting in energy loss as well as threats to the environment [2], [3]. 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 [4]. The presence of dissolved crude oil in water poses significant environmental hazards to aquatic lives. Components of dissolved oil, BTEX which are carcinogenic can cause cancer after a long time of exposure [5]. The awareness of the impact of spilled crude oil and products from it on human health and environment is on the increase [6]. This increasing concern about the pollution of environment by organic chemicals arising from naturally occurring ecological events and industrial processes has created a need for the search of new techniques in the removal of these contaminants [7].

Several initiatives have been developed to treat oil spills and its corresponding pollutants from polluted soils and waters. Natural sorbents still prove to be one of the most reliable, rapid, cost effective and readily available method for the removal of spills from polluted waters and reducing its effect on the environment. The major drawback with natural sorbents is the hydrophobic character of the material which can be addressed by modification with hydrophobic materials. For decades now many researchers have focused on the improvement of the potential of natural material to be used as sorbents for oil spillage treatment with significant success. Recently, for example, Keshawy *et al.* [8] synthesized oil sorbent s based on hydroxypropyl cellulose acrylate. Sidik *et al.*, [9] modified oil palm leaves by enhancing its hydrophobicity with lauric acid. Uzojie *et al.*, [4] carbonized groundnut shells and reported its potential as oil spill sorbents. Sorption studies of crude oil on acetylated rice husks were reported by Thompson *et al.* [10]. Sokker *et al.* [11] synthesized hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization and this too was an excellent material. Wang *et al.* [12] reported hydrophobic silica aerogel (Cabot Nanogel®) to have very attractive crude oil sorption properties. Mowla *et al.* [13] mixed organoclays with sand and reported a breakthrough. Franco *et al.* [14] functionalized alumina nanoparticles with vacuum residue. Karakasi *et al.* [15] modified the surface of high calcium fly ash for its application as sorbents. Organoclays are nanoclays usually of smectite/bentonite type whose interlayers have been modified by intercalation with hydrophobic organic groups. The modification of clay materials at the nano-scale perhaps received a greater interest in recent past to employ it in several waste water treatment methods [16]. In this present study, the authors have converted three types of Nigerian bentonite nanoclays to organoclays for by intercalation with Hexadecyltrimethylammonium Bromide using the hydrothermal method under mild conditions. Time and oil concentration dependence were tested for the three organoclay types and the experimental data gotten was tested kinetic and equilibrium models to describe the manner and mechanism of the sorption procedure. The aim of this study is to investigate the sorption pattern of crude oil on synthesized

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organoclays and recommend them as environmentally friendly and cost effective materials for environmental remediation.

2 MATERIALS AND METHODS

2.1 Materials

Samples of crude oil were collected from the Nigerian National petroleum company, NNPC (Kaduna refinery). The samples were weathered in air for 24 hours using the methods of Hussein *et al.* [17], to remove volatile organic compounds thereby stabilizing the crude oil and to remove unwanted solids by sedimentation. Three clays samples gotten from bentonic turfs in Nigeria and coded BentA (Yobe Bentonite), BentB (Borno Bentonite) and BentC (Yola Bentonite). The Hexadecyltrimethylammonium Bromide salt used was supplied by Sigma Aldrich. All other chemicals used were of Analytical Grade and no further purification was carried out before synthesis.

2.2 Organophilization of Bontoite clays

The Clays were synthesized in the laboratory using the methods described in Manocha *et al.* [18]. The clays were first purified to get rid of unwanted metals and organic materials present. The purified clays were intercalated with HDTMA using the hydrothermal method under very mild conditions. The optimum results were gotten at 80°C, 10 hours, using 50% w/w HDTMA. The organophilized samples were dried for 24 hours in a laboratory oven at 80°C, pulverized, sieved with 200µm mesh sieves and kept in air tight containers for further purification. The optimum conditions obtained from this preliminary analysis were then applied to study the equilibrium and rate sorption experiment at various initial oil concentrations. Three of the organoclays have been chosen for this study, OCA, OCB and OCC synthesized from BentA, BentB and BentC respectively.

2.3 Sorption Studies

The sorption of oil from water was carried out using the Choi and Cloud [19] method with some modifications, where 0.5g each of the organoclays were placed in 250 mL beakers containing about 5g of crude oil displaced in 100 ml water at 24°C. The samples were left in the mixture for 10mins with little agitation. The sorbents were then removed from the beakers using sieving nets. The nets were allowed to drain and then the oil sorption capacity (OSC) of the organoclays determined. To study the effect of crude oil initial concentration, the concentrations of crude oil in the beakers were varied from 0.5 to 5g/100ml of water. Equilibrium isotherms were obtained by plotting a graph of the OSC versus the initial oil concentration for both the nanoclays and the organoclays. The effect of contact time was also studied by varying the contact time on the sorption uptake using constant weights of both crude oil and sorbents. To explain the kinetic behaviour of crude oil on the organosorbents, this kinetic data obtained were further treated with the linear expressions of the pseudo-second-order rate model, the Elovich kinetic model and the Weber and Morris Intraparticle Diffusion model. The Langmuir, the Freundlich and the Weber and the Dubinin-Radushkevich isotherm models were used to explain the interaction and nature of sorption between the sorbed oil and the initial oil concentrations of the crude oil.

3 RESULTS

The characteristics of the clays used are shown in Table 1.

3.1 Effect of Initial Oil Concentration Studies

The initial concentration study is very important because the initial concentration of the oil residue in solute can strongly affect the sorption kinetics and more specifically, the mechanism that controls the overall kinetic coefficient [11]. Fig.1 explains the relationship between initial concentration and the amount of oil sorbed by the nanoclays, hence showing the effect of initial oil concentration on the sorbents. The plots show that the sorption of oil increases with increasing initial oil concentration up to a certain level and attains equilibrium. It is also evident from the Fig.1 that the sorption capacities of the organobentonites were higher than those of the raw nanoclays. This is because the nanoclays are naturally hydrophilic. The raw clays also easily form dispersions in the water and later settle at the base of the beaker after a while, making sorption of the oil difficult. The high sorption capacity of organobentonite is due to the presence of hydrophobic groups from the quaternary ammonium cations intercalated within the layers of the nanoclays during the organophilization process, hence the enhanced hydrophobic character of the nanoclay particles. This is an indication of success in the intercalation of clays by the surfactant. At higher initial concentrations, the surface of the hydrophobic organoclays enhances oil residue diffusion through the film surrounding the materials and into the porous network of the organoclays [11], [20].

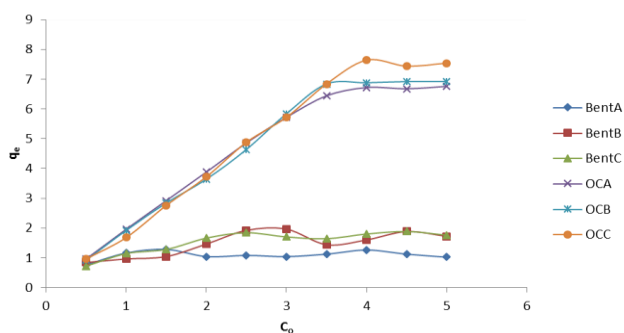


Fig. 1. The effect on Initial oil concentration on sorption.

3.2 Equilibrium Sorption Isotherms

The existence of equilibrium between the liquid and solid phase is well described by sorption isotherms [21]. Equilibrium studies that give the capacity of the sorbent and the equilibrium relationships between sorbent and sorbate are described by sorption isotherms which are usually the ratio between the quantity sorbed and the remaining in solution at fixed temperature at equilibrium [22]. Sorption isotherms are important in describing how solutes interrelate with the sorbents and so is critical in optimizing the use of sorbents [11]. Equilibrium data collected were fitted into the well-known Langmuir, Freundlich, and Dubinin-Radushkevich sorption isotherm models [21], [23] with the assumption of crude oil being a mono-component system and thereby eliminating the possibility of multicomponent competition. These isotherm models are depicted in Figs. 2, 3 and 4. The isotherms yield constants whose values express the affinity of sorbate for the surface of sorbent.

3.2.1 The Langmuir Isotherm Model

The Langmuir Isotherm model which was originally developed to describe the sorption of gas on to solid surface is used for monolayer sorption onto a surface containing a finite number of identical binding sites [24]. The model represents the equilibrium distribution of sorbate molecules between the solid and liquid phases, suggesting the formation of monolayer sorption and also energetically homogeneous surfaces [10], [25], [26]. According to [11], the mechanism of sorption may involve three steps; the diffusion of ions residue to the external surface of sorbent; the diffusion into the pores of sorbent; and the sorption of the residue on the internal surface of sorbent. The first part of sorption could be affected by the initial concentration and contact time. The final step of the sorption is considered as a rate-determining step and as a relatively rapid process. Sorption isotherms of the organoclays were studied using the linearized form of the Langmuir isotherm model expressed as:

$$1/q_e = 1/C_e q_m b + 1/q_m \quad (1)$$

The linearized form of the Langmuir isotherm allows the calculation of sorption capacities and the Langmuir constants by plotting $1/q_e$ against $1/C_e$ as shown in Fig.2. Where q_e is the amount of oil (g) accumulated per gram of organoclay material used; C_e is the residual amount of oil in solution at equilibrium, q_m , a constant related to sorption capacity (mg/g), is the maximum specific uptake for a monolayer coverage corresponding to the site saturation and b the Langmuir constant related to energy of sorption, is the ratio of sorption and desorption rates. The constant b expresses the affinity between the sorbent and sorbate [27]. q_m and b were obtained from the slopes and intercepts respectively of the plots shown in Fig.2. The Langmuir isotherm parameters are given in Table 2. The high values of q_m and the low values of b obtained suggest that the organoclays have high affinity for crude oil and subsequently large organic molecules. The essential characteristics of Langmuir isotherm can be expressed by dimensionless separation factor, R_L [28]:

$$R_L = 1/[1 + bC_o] \quad (2)$$

Where C_o is the highest initial concentration of sorbate ($\text{mg}\cdot\text{l}^{-1}$), and b ($\text{l}\cdot\text{mg}^{-1}$) is the Langmuir constant. The value of R_L indicates the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [29], [30]. The R_L values given in Table 2 for this sorption process were in between 0 and 1, indicating the favourable sorption of crude oil on the organoclays took place. This suggests that the organoclays are suitable sorbents for the pickup of crude oil in water. The R^2 values of the Langmuir Isotherm are all greater than 0.99 and higher than the R^2 values of the Freundlich and D-R isotherms. Indicating that the manner of sorption in monolayer and that the surfaces of the organoclays are predominantly homogeneous.

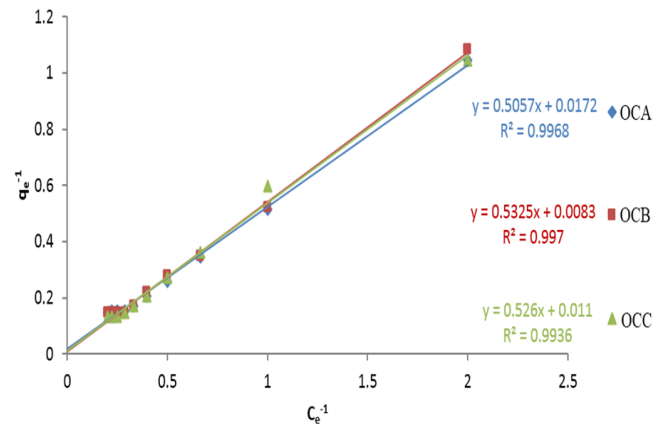


Fig. 2: The Langmuir Isotherm plots

3.2.2 The Freundlich sorption model

The Freundlich isotherm has been applied to estimate the sorption intensity of the sorbent towards the sorbate. One major characteristic of the Freundlich isotherm, though not based on a theoretical background, is its ability to give a good representation of equilibrium data over a restricted range of concentration. The model assumes that the removal of crude oil molecules occurs on a heterogeneous sorbent surface and can be applied to multilayer sorption [31]. The equilibrium data were treated with the linearized Freundlich isotherm by plotting a chart of $\ln q_e$ against $\ln C_e$ as shown in Fig.3. The linearized form of Freundlich sorption isotherm [34] was used to evaluate the sorption data and is represented as:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (3)$$

This isotherm is usually used in special cases of heterogeneous surface energy which is characterized by the heterogeneity factor $1/n$. n is an empirical parameter related to the sorption intensity, where q_e is the solid phase sorbate concentration at equilibrium (g/g), C_e is the liquid phase sorbate concentration at equilibrium (g/L), K_F is a constant describing the sorption capacity (L/g), also called the Freundlich constant. A plot $\ln q_e$ vs. $\ln C_e$ enables the constant K_F and exponent $1/n$ to be determined. The calculated Freundlich isotherm parameters obtained are given in Table 2. The values of the constants n and K_F were obtained from the slope and intercept respectively. The magnitude of K_F and n shows easy separation of the crude oil from the polluted water and high sorption capacity. The values of K_F and n determine the steepness and curvature of the isotherm. The n values should be in between 1 and 10 for favourable sorption. In the present study values of n which is related to the distribution of bonded molecules on the organoclay surface were found to be positive and between 1 and 10 for the crude oil sorption. The values of the calculated n were 1.034 for OCA, 1.135 for OCB and 1.088 for OCC which indicates the favourable sorption and also implies that the organoclays have a high affinity for crude oil and therefore the sorption capacity of the organoclays will be high at high sorbent dosages but will rapidly diminish at lower dosages of sorbent. Also, the higher the K_F value, the greater the sorption intensity [22]. The K_F values for OCB (1.966) seemed to be the highest and OCC (1.899) being the runner-up and slightly higher than OCA (1.862). The higher values of K_F indicate more sorption, so the results of OCA offered a maximum sorption capacity compared with the other sorbents. The Freundlich equation is also

suitable for a highly heterogeneous surface and a sorption isotherm lacking a plateau, indicating a multi-layer sorption [32]. Analyses of the values of the regression coefficients (R^2) obtained for these isotherm plots reveal that Freundlich isotherm also describes the present system's sorption pattern as heterogeneous surface but within a restricted range only. The R^2 for each organoclay were high but relatively much lower than their corresponding Langmuir and Dubinin-Radushkevich values. This shows that this isotherm gave a good but not a better fit to the experimental data compared to the Langmuir and Dubinin-Radushkevich isotherms. The results support the findings in the Langmuir Isotherm studies that the organoclays surfaces are predominantly homogenous.

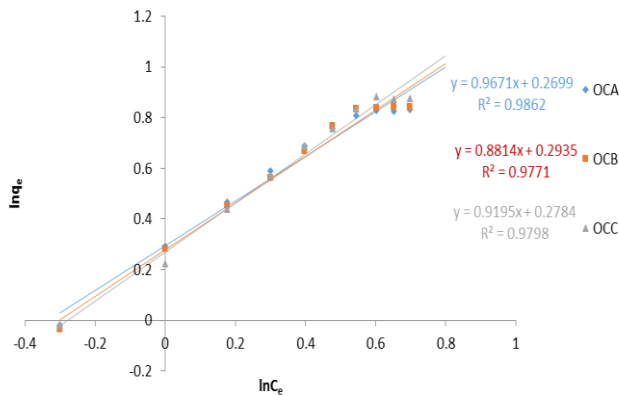


Fig. 3: The Freundlich Isotherm chart

3.2.3 The Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich isotherm (D-R) is a very popular model for a single solute system, based on the distribution of solute between the solid phase and aqueous phase at equilibrium [33]. The D-R isotherm model was applied to the data in order to deduce the heterogeneity of the surface energies of sorption, the characteristic porosity of the sorbent and the apparent sorption energy [22], [34]. The linear form of the D-R isotherm is expressed as:

$$\ln q_e = \ln q_D - 2B_D RT \ln(1 + 1/C_e) \quad (4)$$

Where, B_D ($\text{mol}^2 / \text{J}^2$) is a constant related to the mean free energy of sorption per mol of the sorbate as it migrates to the surface of the sorbent from infinite distance in the solution and the constant q_D (mol/g) is the D-R isotherm constant representing the theoretical saturation capacity or the degree of sorbate sorption by the sorbent surface. Usually, R is the ideal gas constant, (8.314J/molK), T (K) is the temperature of sorption and E (kJ/mol) is the mean free energy of sorption per molecule of the sorbate. Plots of $\ln q_e$ versus $[RT \ln(1 + 1/C_e)]$ as shown in Fig.4, yielded straight lines and indicate a good fit of the isotherm to the experimental data. The coefficient of Regression- R^2 , the apparent sorption energy- E , and the values of q_D and B_D are summarized in Table 2. The constants q_D and B_D were calculated from the intercept and slope respectively. E was calculated using $E = 1/(2B_D)^{1/2}$ when transferred to the surface of the solid from infinity in solution [35]. The higher the values of q_D , the higher the sorption capacity and the better are the biosorbents [22], [36]. The q_D values were in the order, OCC (14.51) > OCB (12.56) > OCA (11.92). This implies that the OCC is a better sorbent than the OCB which is consequently better than OCA. When the value

of E lies below 20kJ/mol it indicates a physical sorption process [37], [38]. The values of the apparent energy of sorption (E) were above 20kJ/mol for all instances and indicated that chemisorption predominated physisorption between the organoclays and the crude oil molecules. As indicated from the plots, the value regression parameter- R^2 of the D-R isotherm is relatively higher than those of the Langmuir and Freundlich Isotherms. R^2 (0.0.9915-OCA, 0.9792-OCB and 0.9915-OCC) indicates suitability of the D-R isotherm on the equilibrium uptake data and proves a better choice in explaining sorption energies.

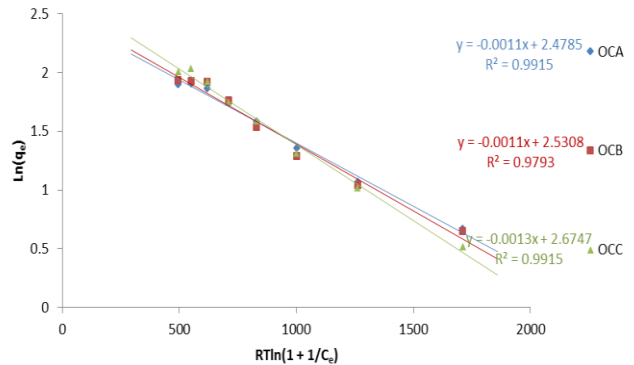


Fig. 4: The Dubinin-Radushkevich model for organoclays.

TABLE 2
PARAMETERS DESCRIBING THE EQUILIBRIUM ISOTHERM MODELS

Model	Freundlich		Langmuir			Dubinin-Radushkevich				
	R^2	n	K_F	R^2	Q_m	R_L	q_D	R^2	$B_D \times 10^4$	E
OCA	0.9862	1.0340	1.8617	0.9968	1.9775	0.855	11.923	0.9915	5.5	30.15
OCB	0.9771	1.1346	1.9656	0.997	1.8779	0.928	12.564	0.9793	5.5	30.15
OCC	0.9798	1.0876	1.8985	0.9936	1.9011	0.905	14.508	0.9915	6.5	27.74

3.3 Time Dependent studies

The effect of time on the sorption of oil by the nanoclays was studied by varying the time used in the sorption of the crude oil from water. The relationship between the oil uptake per gram of raw and modified nanoclays (q_t) as a function of the contact time (t) from 1-30 minutes is illustrated in Fig.5. As expected, the plots show that the sorption capacity (q_t) of crude oil increases rapidly with increasing time, t . The plots of the effect of time on oil sorption show that sorption capacity slightly increases with the contact time for the first 1 minute after which there is slow oil removal from the solution was observed. The sorption process was rapid at the initial stages of the contact period and thereafter it became slower towards equilibrium. The sorption sites become less available as the contact time increased, resulting in a slow sorption phase. This phenomenon was due to the fact that a large number of vacant surface sites and microscopic voids were available for sorption during the initial stages, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [11], [39], [40]. During the slow sorption phase, the breakage of oil droplets increased the interfacial area available for sorption [41]. As time goes by, the sorbed oil residue starts to clog the pores near the outer surface so oil

residue can no longer diffuse to the active sites deep within the interior surface. It is also evident from the plots of Fig.5 that the sorption capacities of the organobentonites were higher than those of the raw nanoclays. The difference in the sorption behaviour of the sorbent groups is ascribed to the hydrophilic character of the surface properties. The hydrophilic surfaces of nanoclays give them affinity towards water, making them easily form dispersions in the water and later swelling at the base of the beakers after some moment, making sorption of the oil difficult. This is because the liquids are held on surfaces either within the sorbent material such as pores, capillaries of interstices, or on external surfaces of plastic fibres or mineral granules. Also, the small interlayer spacing of the clay structures may not allow the oil particles to be trapped by the clay material as the oil droplets are usually larger than the pores sizes of the raw clays and cannot be trapped in the layers of the clays unlike those of the modified clays [39]. This is somehow logical, regarding that a molecule cannot enter a pore which is smaller than the molecule itself. The higher sorption capacity of the modified clays are as a result of the effect of the available surface area subjected to the oil [10], and the ability for the oil molecules to form covalent bonds with the alkylammonium cations on the surface and interlayers of the organoclays. Sorption is a surface phenomenon that is directly related to surface area. Therefore increasing the surface area increases the specific sorption. As the basal spacing of the clay expands, it increases the surface area of the materials and as the surface area increases, it increases the capillaries that are being formed and hence increases/favours absorption [42], [43]. The hydrophobic character of the modified clays was due to successful intercalation of the ammonium quaternary cation of HDTMA within the layers of the clays. These results are consistent with the findings of other researchers [10], [42], [44] in the sorption of oil by hydrophobic and hydrophilic porous materials. This is evidence that the organobentonites are suitable materials for the removal of oil from oil-water interactions.

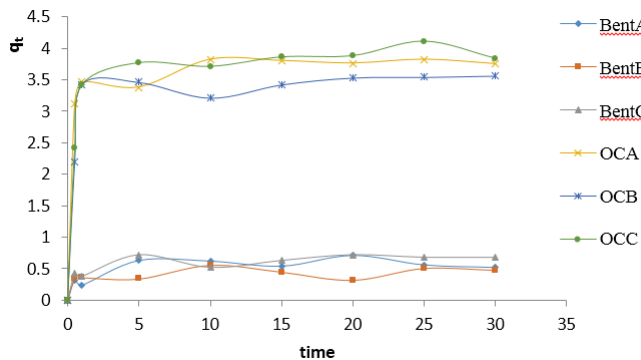


Fig. 5: The effect of time on sorption of crude oil by raw and modified clays

3.4 Sorption Kinetics

Sorption is a mass transfer process involving transfer of sorbate from liquid phase into solid phase, and it includes 3 steps: (i) Boundary layer mass transfer across the liquid film around the particle, (ii) Internal diffusion or mass transport within the particle boundary as pore and or solid diffusion, (iii) Sorption within the particle and or on the external surface [45], [46]. The studies of sorption kinetics are important in determining the effectiveness of sorption; however, it is also necessary to identify the types of sorption mechanism in a

given system [47]. The three kinetic models chosen in this study are adequate to determine the kinetic mechanism behind the crude oil sorption by the organoclays.

3.4.1 The Pseudo-Second-Order Rate Model

The data for the time dependent studies of oil sorption on the organoclay samples were subjected to the Pseudo-second-order rate model equation of [48]. This equation is based on the sorption capacity, it predicts the behaviour over the whole range of studies supporting the validity, and is in agreement with chemisorption being the rate-controlling [48]. Based on equilibrium sorption, the pseudo-second-order kinetic model equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (5)$$

Where q_t (mg/g) is the amount of sorbate retained at time, t (min). Plots of t/q_t versus t for the organoclay samples are presented in Fig.6. The value of the sorption capacity of the organoclays q_e , the pseudo-second-order rate constant k_2 (g/mg min), the initial sorption rate constant h (mg/g min), and the coefficient of determination R^2 were evaluated from the plot and presented in Table 3. The constants k_2 and h were calculated respectively from the intercept and slope of the linear plots obtained. The straight lines in the plots prove a good agreement of experimental data with the second-order kinetic model. According to Ho *et al.* [49], if the plot is linear, then the sorption process may be described as chemisorption. The data confirms that modification by HDTMA enhances the equilibrium sorption capacity of the clay materials towards the crude oil. It can be seen that the kinetics of crude oil sorption onto organoclays follow this model with correlation coefficients higher than 0.99. These results imply that chemisorption mechanism plays an important role for the sorption of crude oil on the organoclays. The sorbed oil droplets are held to the surface of the organoclays by covalent forces of the same general type as those occurring between bound atoms in the oil molecules [50].

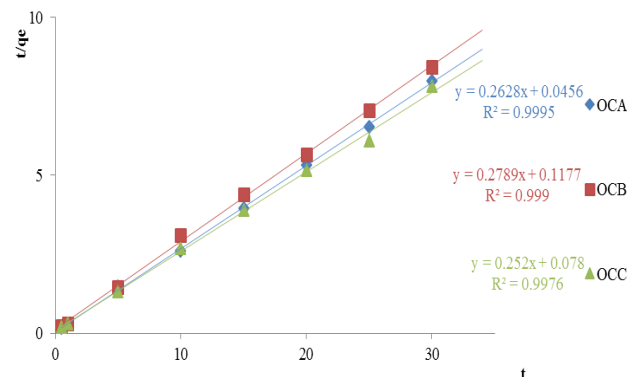


Fig. 6: The Pseudo-second-order rate equation model

3.4.2 The Elovich Model

The possibility that the sorption was occurring in the system water/oil/organoclay, also involving the participation of some other forces, beside the regular Van der Waals forces, has been estimated by applying the Elovich equation [51]. The Elovich equation can be used to describe the kinetic process assuming that the actual organoclay surfaces are energetically heterogeneous though the equation does not propose any

definite mechanism for sorbate–sorbent reactions [47], [52]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [51], [53]:

$$q_t = \alpha \ln \alpha + \alpha \ln t \tag{6}$$

Where α is the initial sorption rate (mg/gmin), and the parameter a is related to the extent of surface coverage and activation energy for chemisorption (g/mg). α and a were calculated from the intercept and slope of the straight-line plots of q_t against $\ln t$. The kinetic data were plotted in Fig.7 and the parameters listed in Table 3. From Table 3, good correlation among the experimental points and the theoretical lines is observed. It implies that the Elovich model well describe the kinetic data over a short period of time. When the correlation between the sorption capacity and the constant b is negative, it is accepted that the adsorbent does not retain the sorbate. The positive value of the constants gives evidence for occurring of sorption. R_E^2 values for OCA, OCB and OCC were 0.9700, 0.9156, and 0.9504 respectively, agreeing with the results of the Pseudo-second-order rate model. The initial sorption rates were 3.49, 3.01 and 2.24 mg/gmin respectively. Showing the OCA is a slightly better sorbents than OCB and OCC. Consequently, the number of active sites available for sorption was reduced due to a large number of sorbate molecules at higher initial concentrations [54]. The applicability of the simple Elovich equation for the present kinetic data indicates that the Elovich equation was able to describe properly the initial kinetics of the crude oil sorption on the surface of the organoclays.

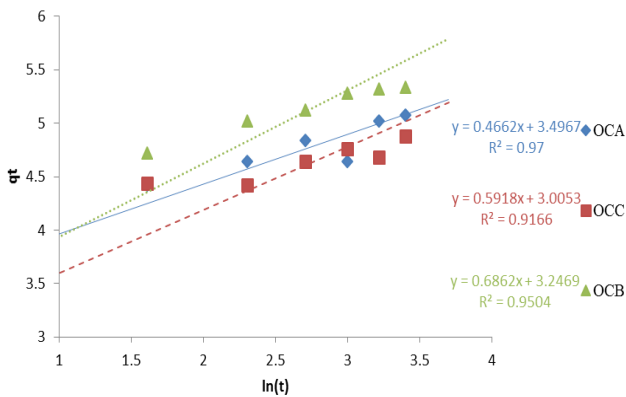


Fig. 7: The Elovich model

3.4.3 The Intraparticle Diffusion Model

Intraparticle diffusion is a transport process involving movement of species from the bulk of the solution to the solid phase [51]. The possibility that the diffusion might be the rate limiting stage in regard to the entire process was evaluated by the linear dependence on the Weber-Morris [55] Intraparticle diffusion model. The pseudo-second-order and Elovich kinetic models are not sufficient to fully describe the sorption mechanism because they cannot identify the diffusion mechanism. The kinetic data were therefore fitted into the equation of the diffusion models developed by Weber and Morris [55]:

$$q_e = k_{id} t + C_i \tag{7}$$

A plot of the amount of sorbate sorbed, q_t (g/g) and the square root of the time t , gives the rate constant k_{id} ($gg^{-1} min^{-1/2}$) which

is the intraparticle diffusion rate coefficient as the slope of the plot and C_i (g/g) which is the intraparticle diffusion coefficient as the intercept of the line accounting the bonding effect between the clay layers. The structure of the solid and its interaction with the diffusion substance influences the rate of transport. Larger k_{id} values illustrate better sorption which is related to improved bonding between sorbate and sorbent particles [56] and may simply be due to higher sorbate concentrations which adds to a greater driving force for diffusion of sorbate molecules into the pores [29]. The organoclays are in the form of porous barriers and the oil droplets move by diffusion from one the aqueous body to the organoclays by virtue of concentration gradient [57]. K_{id} of 0.124, 0.186 and 0.2138 $g/gmin^{-1/2}$ were calculated for OCA, OCB and OCC respectively. This implies that OCC supports an enhanced rate of adsorption more than OCB and OCA and is in turn linked to improved bonding as noted by Itodo *et al.* [56]. The correlation coefficients (R^2) for the intraparticle diffusion model were 0.7137, 0.5341 and 0.582 for OCA, OCB and OCC respectively (Table 3). These relatively poor values of R^2 suggest that intraparticle diffusion may not be the only rate limiting step in the procedure. According to Itodo *et al.* [58], the sorption mechanism assumes intraparticle diffusion if the following conditions are met: (i) High R_2 values to ascertain applicability (ii) Straight line which passes through the origin for the plot area qt vs. $t^{1/2}$. (iii) Intercept $C_i < 0$. A validity test which deviates from (ii) and (iii) above shows that the mode of transport is affected by more than one process which means that two or more stages occur. It is evident that the straight lines did not pass through the origin i.e. $C_i > 0$ for all cases, further indicating that the intra-particle diffusion is not the only rate-controlling step.

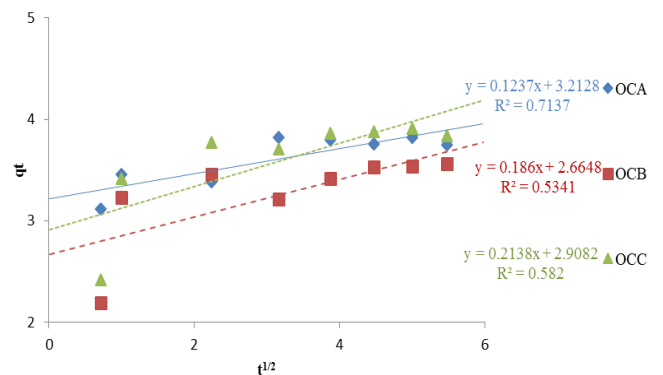


Fig. 8: Intraparticle Diffusion model

TABLE 3
PARAMETERS DESCRIBING THE KINETIC MODELS

Model	Elovich		PSOR			WMDM			
	R_E^2	α	a	R^2	Q_e	k	R_f^2	K_{id}	C_i
OCA	0.9700	3.4967	0.3268	0.9995	3.8052	1.5146	0.7137	0.1237	3.2128
OCB	0.9166	3.0053	0.4052	0.9990	3.5856	6.6088	0.5341	0.186	2.6648
OCC	0.9504	3.2469	0.3805	0.9976	3.9683	0.8142	0.582	0.2138	2.9082

4 CONCLUSION

The values of the kinetic and equilibrium isotherm model suggests that the organoclay materials are good sorbent for the cleaning up of oil spills from aqueous bodies. The sorbent showed a rapid oil sorption and a theoretical sorption capacity sorption capacity of approximately 2g oil/g sorbent. Which is equivalent to four times the weight of the organoclays. A comparison of the results of the coefficients of regression R^2 from Tables 2 and 3 show that the adsorption process is mostly monolayer and the manner of adsorption is by chemisorption. This low R^2 values of the WMID model also suggested that intraparticle diffusivity may not have been the only rate limiting step in the sorption procedure. The results showed that the sorption of crude oil by the synthesized Nigerian organoclays was feasible, suggesting an environmentally friendly and cost effective solution to cleaning oil polluted waters.

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