CORNCOB AS A SORBENT FOR CRUDE OIL AND ITS LOWER FRACTIONS

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ABSTRACT

This study reports oil sorption capacity, sorbed oil recoverability and sorbed oil retention of corncob and a standard: conventional synthetic sorbent used in the oil industry to clean oil spill. The result of the study shows that corncob has lesser oil sorption capacity and sorbed oil recoverability than the standard, but higher sorbed oil retention than the standard. Corncob sorbed per unit mass 3.30 ±0.49 g of crude oil, 2.90 ±0.99 g of diesel and 2.50 ±0.72 of kerosene, while, the standard sorbed per unit mass 11.50 ±0.54 g of crude oil, 10.35 ±0.77 g of diesel and 8.20 ±0.93 g of kerosene. Sorbed oil recovered from corncob and standard are 2.00 ± 0.55 g of crude oil, 1.90 ± 0. 83 g of diesel, 1.40 ±0.71 g of kerosene and 9.67 ±0.36 g of crude oil, 8.40 ±0.95 g of diesel, 6.50 ± 0.49 g of kerosene respectively. 1.25 ± 0.68 g (37 % of sorbed crude oil), 0.95 ± 0.33 g (32 % of sorbed diesel) and 1.05 ± 0.83 g (42 % of sorbed kerosene) were retained by a unit mass of corncob while 1.83 ± 0.33 g (15 % of sorbed crude oil), 1.94 ± 0.97g(19 % of sorbed diesel) and 1.70 ± 0.89 g (20 % of sorbed kerosene) were retained by a unit mass of the standard. Amount of water sorbed together with each sorbate onto corncob and synthetic sorbent is minimal; 14 ml (2.9 g) for corncob and 6 ml (1.2 g) for the standard. Adsorption isotherm and kinetic studies shows that the sorption process of crude oil, diesel and kerosene onto corncob is by Langmuir model, pseudo second order kinetics, intraparticle diffusion and liquid film diffusion mechanism.Corncob can be applied on land and aqueous environment in oil spill clean-up. Comparatively, corncob is not a very effective oil spill sorbent.

Key words: Corncob, crude oil, diesel, kerosene, oil sorption capacity, sorbed oil recoverability.

INTRODUCTION

Oil spill has devastating consequences on the environment which include damage to vegetation, oiling of beaches and in some cases fire outbreak, dead wildlife, oil covered marshlands and contaminated water (Fingas, 2010). One instance of an oil spill is that which happened some years ago on April 20, 2010; the Deepwater Horizon (DWH) oil spill in the Gulf of Mexico (National Oceanic and Atmospheric Administration, U.S Department of Commerce, 2014). The spill affected and in some cases resulted in loss of biodiversity (National Oceanic and Atmospheric Administration, 2014; Hester *et al.*, 2016;

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Venn-Watson *et al.*, 2015). Due to the effects of oil spill in the environment, oil is usually cleaned after a spill. Oil spill clean-up exercise employs methods such as oil containment, recovery of oil and oil removal. Oil is contained through the application of booms and ancillary equipment, while it is recovered using skimmers, sorbents and manual recovery. *Insitu* burning, chemical agents and biological agents are used for oil removal (Fingas, 2013).

Sorbents which are solid materials or mixture of solid materials are frequently used in oil spill clean-up exercise; they recover liquids through the mechanism of absorption, or adsorption, or both (Thomas, 2010). These sorbents can be natural or synthetic in nature; examples of synthetic sorbents include polyurethane and polyester, while natural sorbents which are categorized into organic or inorganic include talc. Perlite, vermiculite or straw, bark and cotton respectively (Ali *et al.*, 2012; Carmody *et al.*, 2007; Likon *et al.*, 2013; Klavins and Porshnov, 2013). Researchers have recently been researching into agricultural based sorbents for oil spill clean-up because of their biodegradability and low cost (Deschamps *et al.*, 2003; Choi and Cloud, 1992). Among the various sorbents that have been employed for oil remediation, synthetic materials, such as polypropylene and polyurethane, are the most commonly used commercial sorbents due to their oleophilic (oil loving) and hydrophobic (water repelling) properties (Teas, *et al.*, 2001). However, these materials are not biodegradable, which is a major disadvantage. Synthetic sorbents generate solid waste after a clean-up exercise which must be disposed by landfill or incinerated (ITOPF Technical Information Paper, 2014; USEPA, 2016). Landfill disposal is environmentally undesirable, and incineration is expensive (Deschamps *et al.,* 2003; Choi and Cloud, 1992). Therefore, there is a renewed interest in natural sorbents and a wide variety of organic vegetable products, such as rice straw, peat moss, wood and cotton, have been employed as sorbents in oil spill clean-up (Deschamps *et al.*, 2003; Choi and Cloud, 1992) . While hydrophobicity and oleophilicity are primary determinants of successful sorbents, other important factors include retention of oil over time, recovery of oil from sorbents, amount of oil sorbed per unit weight of sorbent, and reusability and biodegradability of sorbent (Choi and Cloud, 1992). The effectiveness of sorbents is determined by assessment, and this assessment entails comparison (Volesky, 2004).

Corncob, a biodegradable, available and abundant agricultural waste is obtained from maize. Maize is grown widely throughout the world with the United States, China and Brazil being the top three maize-producers in the world (Ranum *et al.*, 2014). Maize can be processed into a variety of food and industrial products, including starch, sweeteners, oil, beverages, glue, industrial alcohol and fuel ethanol (Ranum *et al.*, 2014). Maize is the world's most widely grown cereal and more maize is produced annually than any other grain (Olaniyi, 2015). It is the most important staple food in sub- Saharan Africa and Latin America (Olaniyi, 2015). The largest African producer of Maize is Nigeria with nearly 8 million tons (Olaniyi, 2015). Corncob is generated in large quantities in Nigeria and is hardly managed as Nigeria faces the problem of solid waste management.

This study aims to assess the possibility of managing corncob waste by using it to solve another environmental problem, oil spill. The assessment was done by conducting a comparative analysis between corncob and a standard: conventional synthetic sorbent used in the oil industry to clean-up oil spill. The parameters that were studied includes: oil sorption capacity, sorbed oil recoverability, sorbed oil retainability and suitable environment where each material can be applied.

MATERIALS AND METHODS

Sample Collection and Preparation

Corncob was obtained from a corn seller in Asaba, Delta state Nigeria. Crude oil was obtained from Shell Petroleum Development Company, Warri, Delta State, Nigeria, while diesel and kerosene were purchased from a filling station located in Asaba, Delta state Nigeria. Synthetic sorbent used as standard in the study was supplied by Department of Oil Spill Remediation, Shell Petroleum Development Company, Port Harcourt, Rivers State, Nigeria.The corncob was ground using a mechanical blender and sieved through a sieve of 500 µm (35 mesh) and packaged in pre-cleaned containers.

Analysis of Sample

Determination of Equilibrium Sorption Capacity of Crude Oil, Diesel and Kerosene onto Corncob and Synthetic Sorbent.

1 dm^3 of crude oil, diesel and kerosene whose weight had been predetermined were each put in a pre-cleaned 2-dm^3 beaker. The weight of each sorbate was used as the initial concentration.5 g of corncob/synthetic sorbent was weighed and added into the beaker and left for a required contact time at 28°C. The contact times used in this study ranged from 10 to100 mins, at 10 mins interval. At the end of each contact time, the content in the beaker was passed through a sieve of 425 µminto another pre-cleaned and pre-weighed 2-dm^3 beaker and allowed to drain. The weight of the 2-dm^3 beaker containing unsorbed sorbate was weighed and the weight of unsorbed sorbate obtained by weight difference. The weight of the unsorbed sorbate was used as final concentration of each sorbate.

At each contact time the amount of crude oil, diesel and kerosene sorbed onto a unit mass of corncob/synthetic sorbent was calculated from:

$$q = \frac{C_i - C_f}{M}$$

Where q = the amount of oil sorbed onto a unit mass of corncob/synthetic sorbent,

C_i = initial Amount of oil in grams (g),

C_f= final Amount of oil in grams (g),

M = mass of sorbent in grams (g).

or

$$q = \frac{Initial\ weight\ of\ oil - Final\ weight\ of\ oil}{M}$$

From the plot of amount of oil sorbed onto a unit mass of corncob/synthetic sorbent against time, the amount of oil sorbed at equilibrium was obtained.

Determination of Equilibration time of Sorption of Crude Oil, Diesel and Kerosene onto Corncob and Synthetic Sorbent.

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This was obtained from the plot of amount of oil sorbed onto a unit mass of corncob/synthetic sorbent against time, as the time corresponding with the amount of oil sorbed onto a unit mass of corncob/synthetic sorbent at equilibrium.

Determination of Recovery of Sorbed Crude Oil, Diesel and Kerosene from Corncob/Synthetic Sorbent

The amount of sorbed crude oil, diesel and kerosene recovered from corncob/synthetic sorbent was determined by removing each sorbent from the sieve, weighing it and afterwards subjecting it to pressing using a carver hydraulic press (Model M, serial No. 12000 – 137) operated at a pressure of 25 tonnes, for 5 mins, at 28°C. After pressing, the sorbent was re- weighed and the weight of sorbate recovered was determined by weight difference.

The amount of sorbed crude oil, diesel and kerosene recovered per unit mass of corncob/synthetic sorbent was determined from the expression:

$$q = \frac{Initial\ weight - Final\ weight}{Mass\ of\ sorbent}$$

The experiment was performed in triplicate and the average and standard deviation were calculated and used.

The amount of sorbed oils retained per unit mass of corncob/synthetic sorbent was obtained from the expression:

$$q = Q_1 - Q_2$$

Where

Q_1 = Quantity of oil sorbed per unit mass of corncob/synthetic sorbent

Q_2 = Quantity of sorbed oil recovered per unit mass of corncob/synthetic sorbent.

Determination of the sorption Process of Crude Oil, Diesel and Kerosene onto corncob/Synthetic Sorbent Using Adsorption Isotherm.

The adsorption models applied to determine the sorption process of crude oil, diesel and kerosene onto corncob/synthetic sorbent are the linearized form of Langmuir, Freundlich, Elovich, Temkin and Dubinin-Radushkevich adsorption models. Five different initial amounts of crude oil, diesel and kerosene were used to obtain different values of equilibrium sorption capacity (q_e) and equilibrium concentration (C_e). The experiment was conducted as mentioned above. The sorbate – sorbent system was left to contact for one hour. The experiment was conducted in triplicate for each initial concentration and the average taken.

Kinetic Studies

Lagergren pseudo-first-order, pseudo-second-order, intraparticle diffusion and liquid film diffusion models were the kinetic models applied to the experimental data to investigate the rate and mechanism of crude oil, diesel and kerosene sorption onto corncob and synthetic sorbent.

Determination of Sorption of Crude Oil, Diesel and Kerosene Displaced on Water, Onto Corncob and Synthetic Sorbent.

To ascertain the mopping behaviour of corncob and synthetic sorbent when crude oil, diesel and kerosene spill on water, the experiment was repeated. 1 dm^3 of water was poured into a pre-weighed 2-dm^3 beaker and weighed; the weight of water was obtained by difference in weight. 0.5 dm^3 of oil whose initial weight had been predetermined was added into the water in the beaker. 5 g of corncob/synthetic sorbent was weighed and added into the oil/water mixture and left for a contact time of 100 mins.

Fourier Transform Infrared (FTIR) Spectroscopic Analysis of Standard (Conventional Synthetic Sorbent)

The functional groups present in the standard were determined by FTIR spectroscopy. The FTIR analysis was carried out using SHIMADZU FTIR-8400S spectrophotometer with a NaCl cell.

RESULTS

Figure 1 showsthe amount of crude oil, diesel and kerosene sorbed onto corncob and the standard. From the figure, the equilibrium sorption capacity of the sorbates onto a unit mass of corncob, which is the oil sorption capacity of corncob, was 3.30 ± 0.49 g of crude oil at 60 minutes, 2.90 ± 0.99 g of diesel at 60 minutes and 2.50 ±0.72 g of kerosene at 60 minutes. The equilibrium sorption capacity of the sorbates onto a unit mass of synthetic sorbent was 11.50 ± 0.54 g of crude oil at 40 minutes, 10.35 ±0.77 g of diesel at 40 minutes and 8.20 ± 0.93 g of kerosene at 40 minutes. FTIR spectrum of the synthetic sorbent is shown in Fig. 2, the prominent peaks indicate that it is a long chain hydrocarbon; 829.42cm^{-1} (s) C=C (def) of alkene, 983.73 cm^{-1} (s) C=C (def) of alkene, 1159.26 cm^{-1}, (s) C-C (str) of alkane, 1369.50 cm^{-1} (s) C-H (def) for alkanes, 1453.41 cm^{-1}(s) C-H (def) for alkanes, 2925.15 cm^{-1}(s) C-H (str) of alkane.

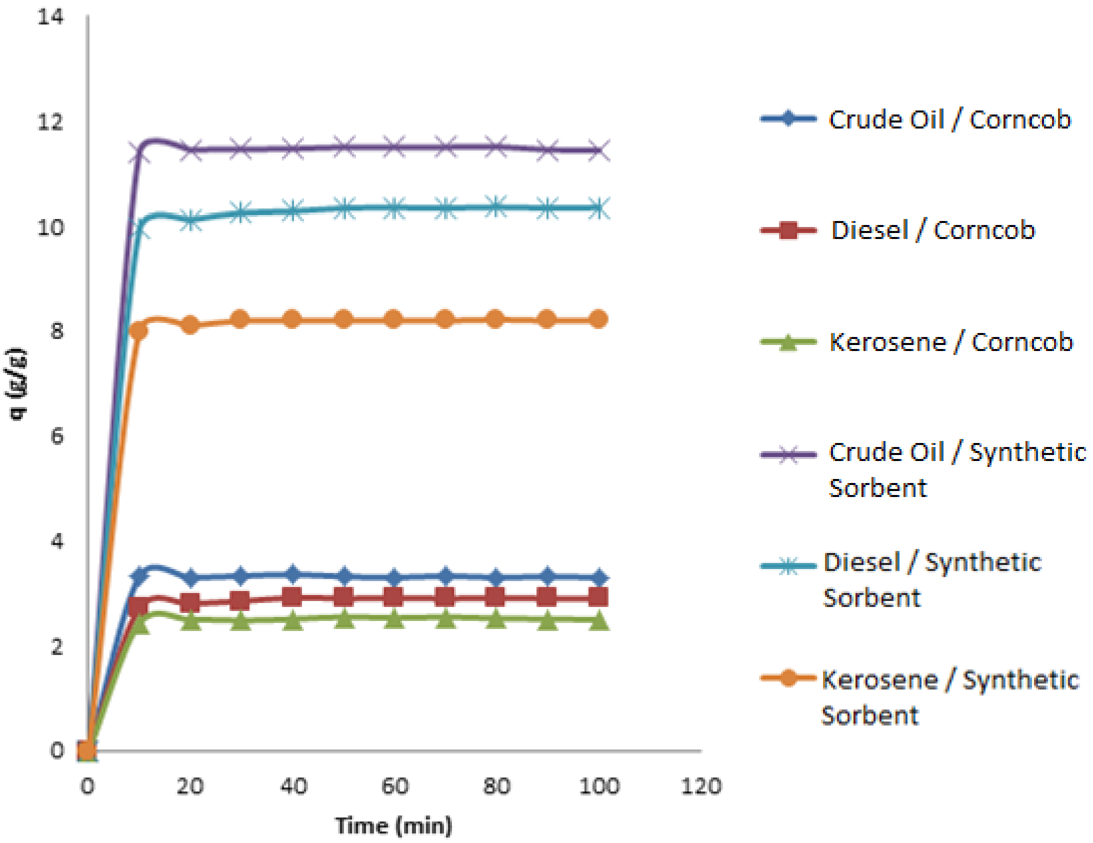

Figure 1: Amount of crude oil, diesel and kerosene sorbed onto a unit mass of corncob/ synthetic sorbent against time.

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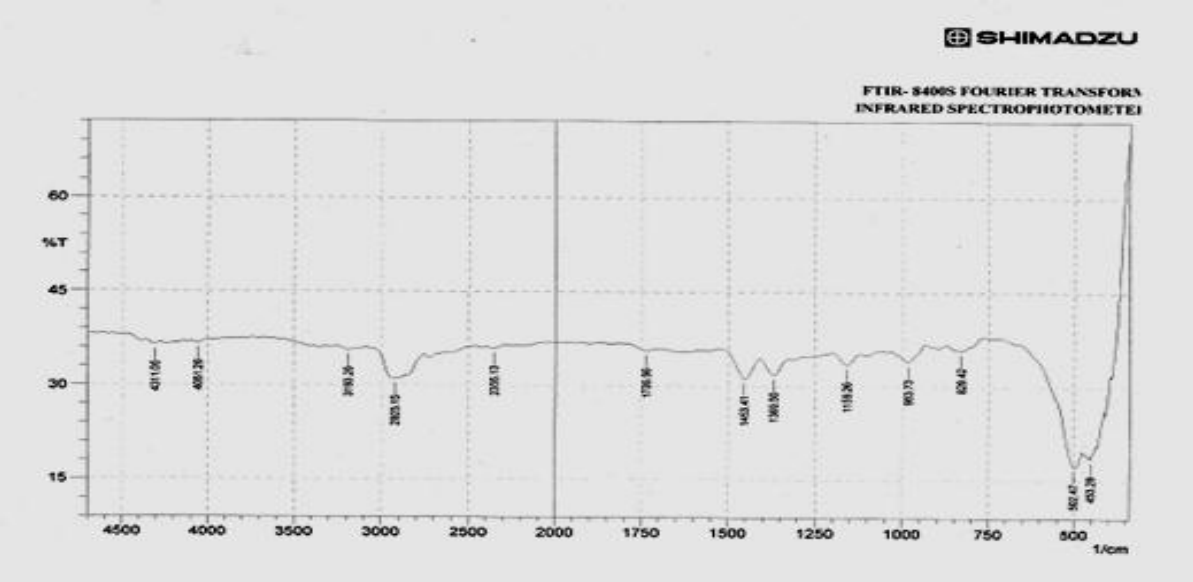

Figure 2: FTIR spectrum of synthetic sorbent.

The linearized form C_e/q_e versus C_e of the Langmuir adsorption isotherm produced the best fit isotherm (0.99) for sorption of crude oil, diesel and kerosene onto corncob and synthetic sorbent, this result is presented in Fig. 3.

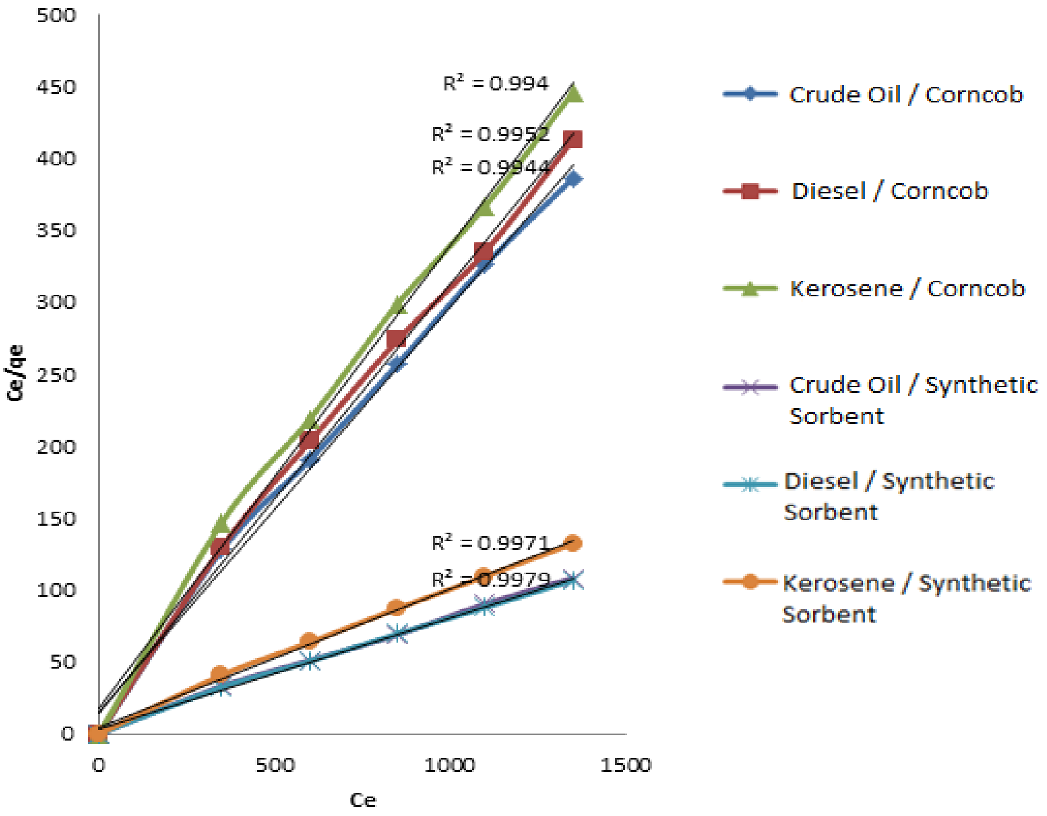

Figure 3: Langmuir Ce/qe versus Ce of sorption of crude oil, diesel and kerosene onto corncob/synthetic sorbent.

Table 1: Parameters of Langmuir isotherm (C_e/q_e vs C_e), equilibrium sorption capacity (q_e) Pseudo first and second order of crude oil, diesel and kerosene onto corncob and synthetic sorben.

Sorption type	b($L\ g^{-1}$) (Langmuir isotherm)	q_m ($g\ g^{-1}$) (Langmuir isotherm)	r^2 (Langmuir isotherm)	q_e($g\ g^{-1}$)	$q_{e,\ exp}$ (mg/g) Pseudo first order	$q_{e,\ Calc}$ (mg/g Pseudo first order	R^2 Pseudo first order	$q_{e,\ Calc}$ (mg/g) Pseudo second order	R^2 Pseudo second order
Sorption of crude onto corncob	-1.00	3.60	0.9944	3.30	3300	201.8	0. 0254	3390	0.9999
Sorption of diesel onto corncob	-1.00	2.97	0.9952	2.90	2900	164.0	0.013	2980	0.9999
Sorption of kerosene onto corncob	-1.00	2.55	0.9944	2.50	2500	910	0.3562	2540	0.9997
Sorption of crude oil onto synthetic sorbent	1.00	11.62	0.9955	11.50	11500	121.51	0.998	12500	1.00
Sorption of diesel onto synthetic sorbent	1.00	10.52	0.9979	10.35	10350	735.09	0.9811	10880	1.00
Sorption of kerosene onto synthetic sorbent	1.00	8.40	0.9971	8.20	8200	365.03	1.00	8333.33	1.00

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The amount of sorbed oils recovered from and retained by corncob and synthetic sorbent are shown in Figs. 3 and 4. 2.00 ± 0.55 g of crude oil (60 % of sorbed crude oil), 1.90 ±0.83 g of diesel (65 % of sorbed diesel) and 1.40 ± 0.71 g of kerosene (57 % of sorbed kerosene) were recovered from a unit mass of corncob while 9.67 ± 0.36 g of crude oil (84 % of sorbed crude oil), 8.40 ± 0.95 g of diesel (81 % of sorbed diesel) and 6.50 ±0.49 g of kerosene (79 % of sorbed kerosene) were recovered from a unit mass of synthetic sorbent. The amount of sorbed oils retained by a unit mass of corncob is about 1.25 ± 0.68 g of crude oil (37 % of sorbed crude oil), 0.95 ±0.33 g of diesel (32 % of sorbed diesel), and 1.05 ± 0.83 g of kerosene (42 % of sorbed kerosene), while, 1.83 ±0.33 g of crude oil (15 % of sorbed crude oil), 1.94 ±0.97 g of diesel (19 % of sorbed diesel) and 1.70 ±0.89 g of kerosene (20 % of sorbed kerosene) were retained by a unit mass of synthetic sorbent.

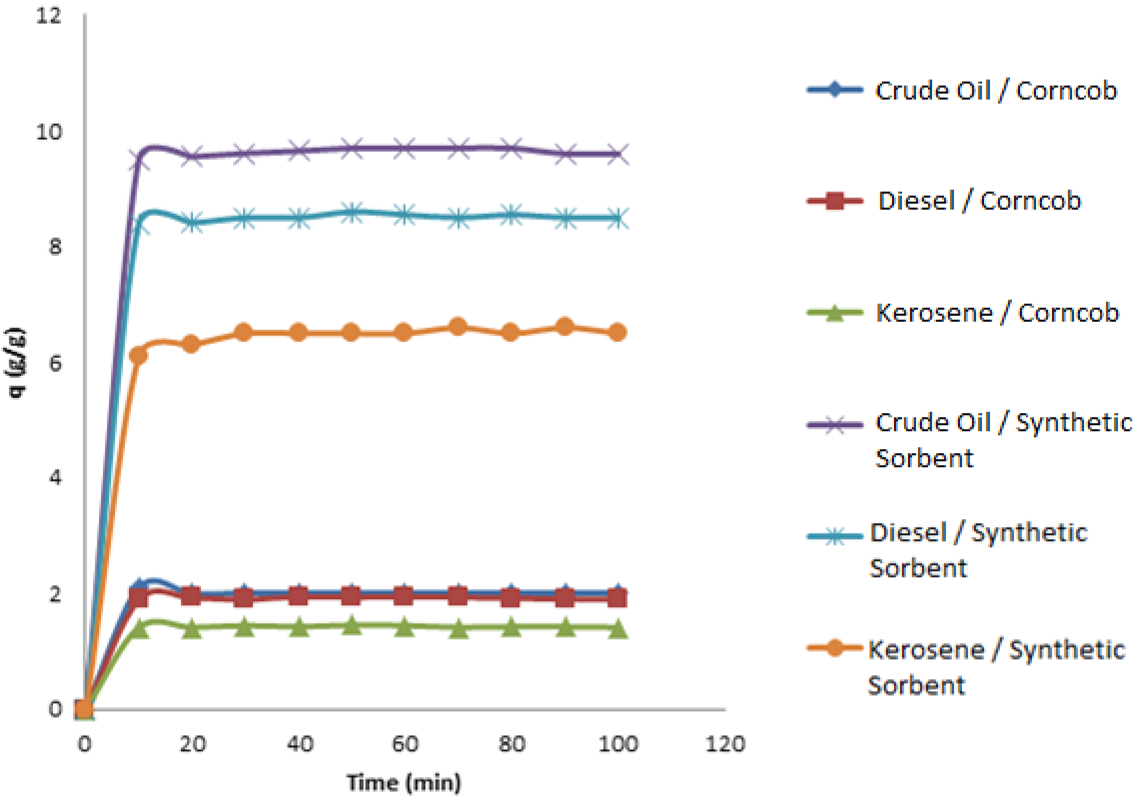

Figure 4: Amount of crude oil, diesel and kerosene recovered from a unit mass of corncob/synthetic sorbent against time.

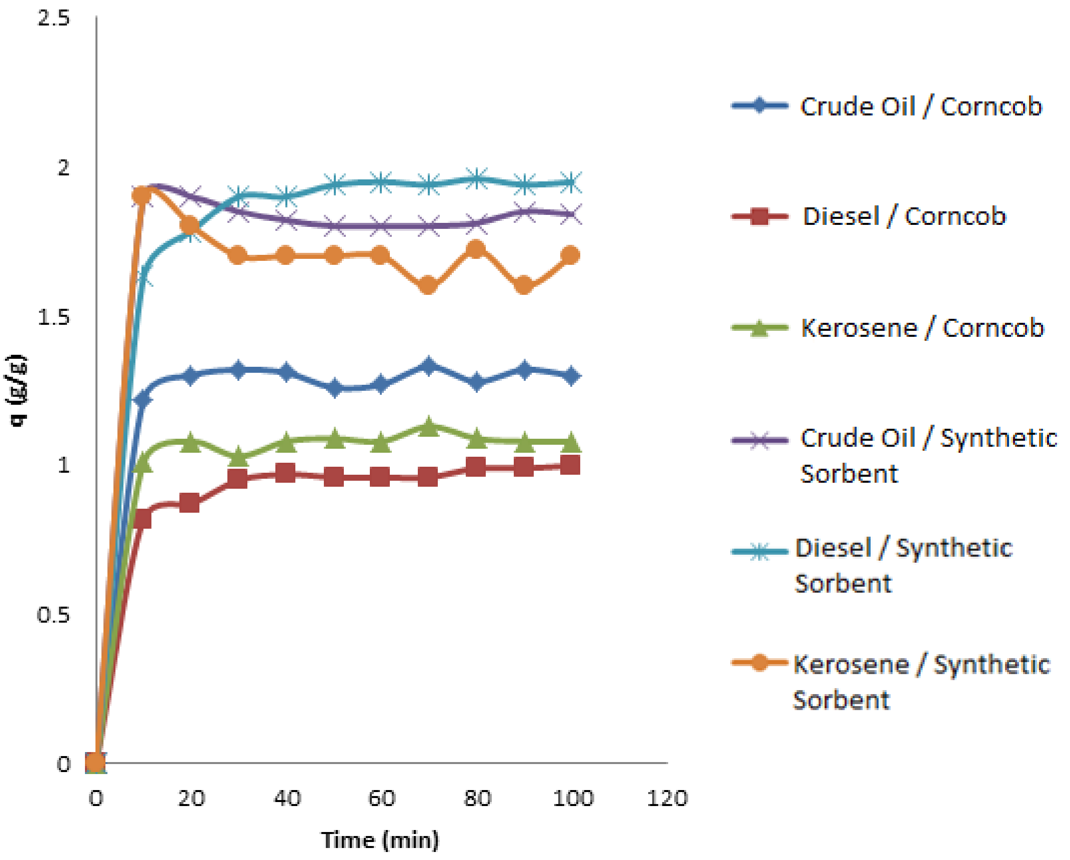

Figure 5: Amount of crude oil, diesel and kerosene retained by a unit mass of corncob/synthetic sorbent against time.

The results of kinetic studies of the rate and mechanism of sorption of crude oil, diesel and kerosene onto corncob and synthetic sorbentare presented in Table 1. The results show that for sorption of the sorbates onto corncob, pseudo first order kinetic model correlation coefficients (R^2) value is low, while it is higher for synthetic sorbent. Pseudo first order calculated equilibrium sorption capacities for both sorbents are lower than the experimental values. Pseudo second order kinetic model correlation coefficient (R^2) and calculated equilibrium adsorption capacities (q_e calc) values of the sorption of the sorbates onto corncob and synthetic sorbent are also presented in Table 1. The R^2 values are between 0.999 – 1.00. Pseudo second order calculated equilibrium sorption capacities for both sorbents are higher than the experimental values.

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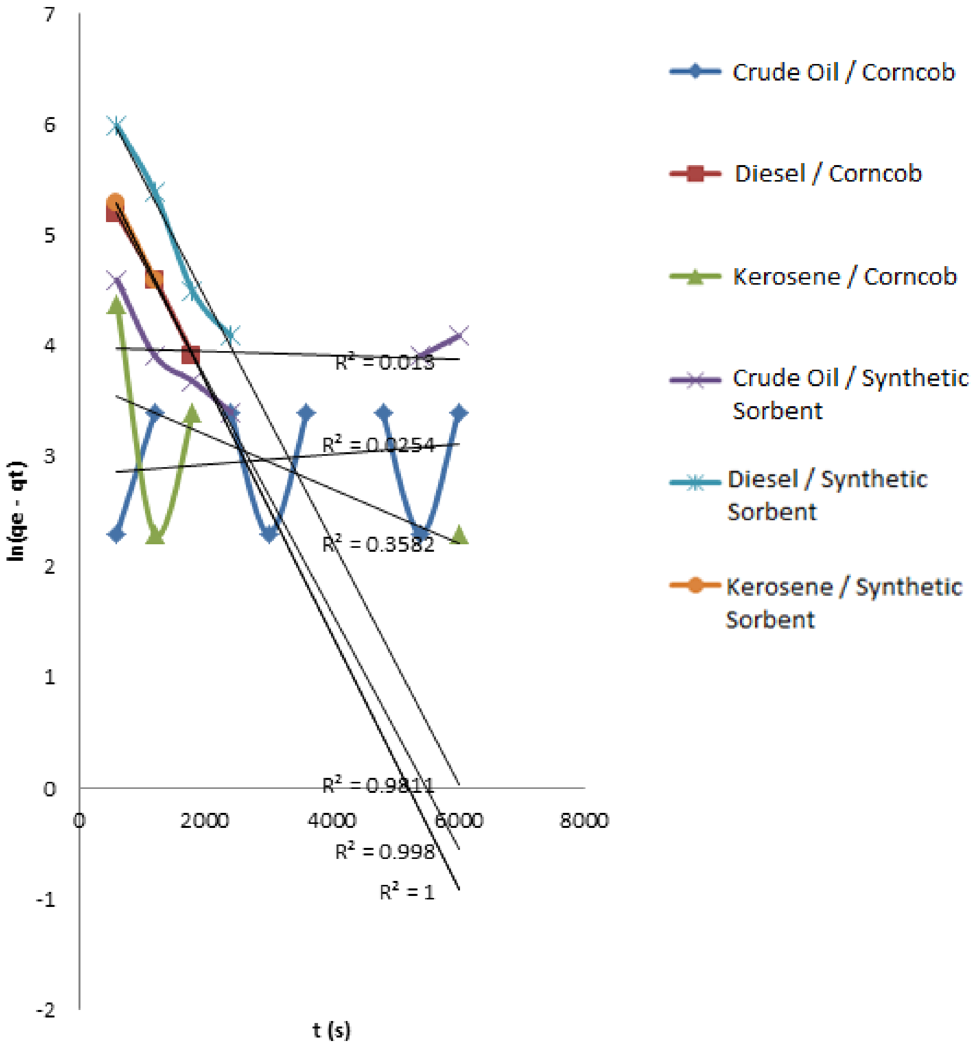

Figure 6: Pseudo first order lnq_e-$q_t$versus t of sorption of crude oil, diesel and kerosene onto corncob/synthetic sorbent.

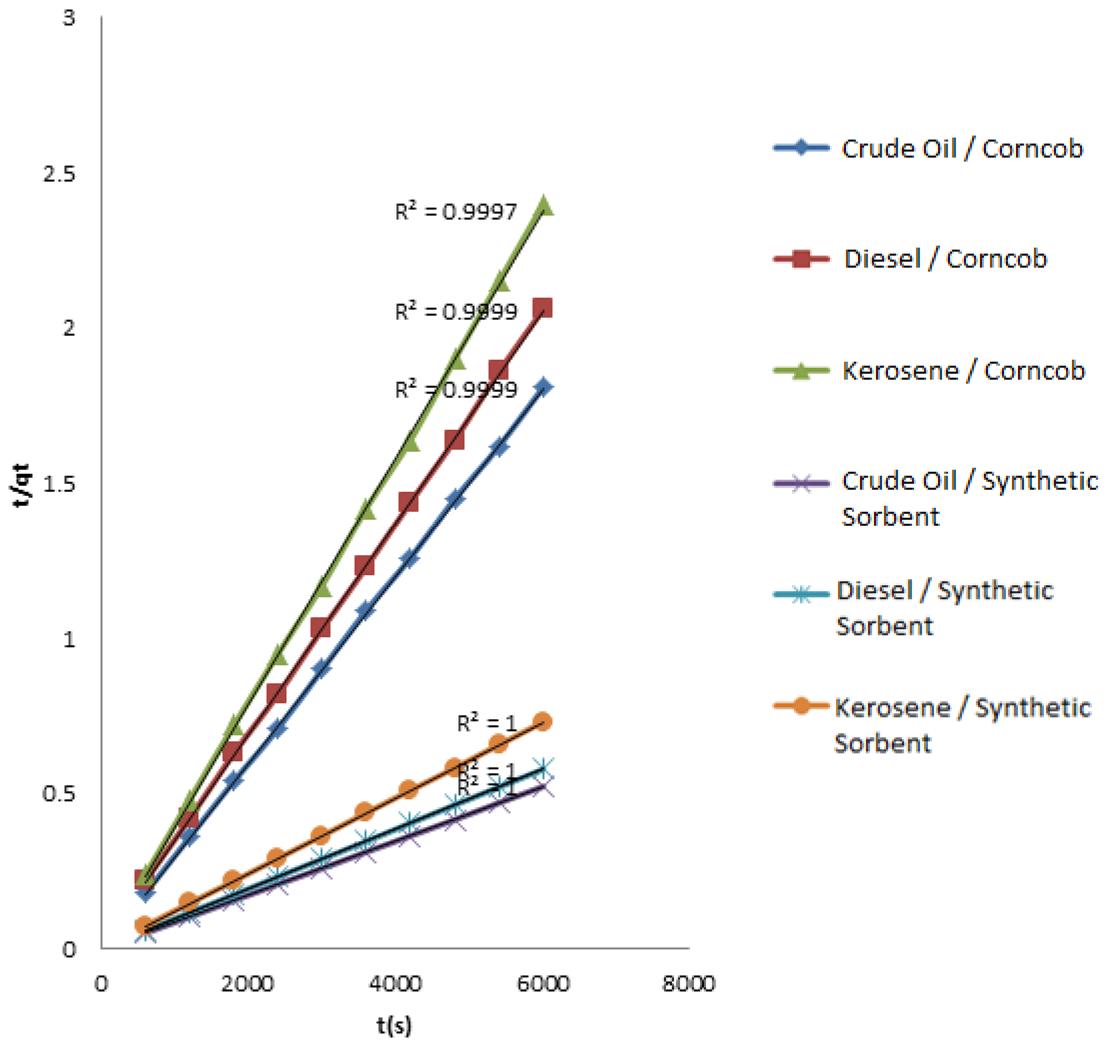

Figure 7: Pseudo second order t/$q_t$versus t of sorption of crude oil, diesel and kerosene onto corncob/synthetic sorbent.

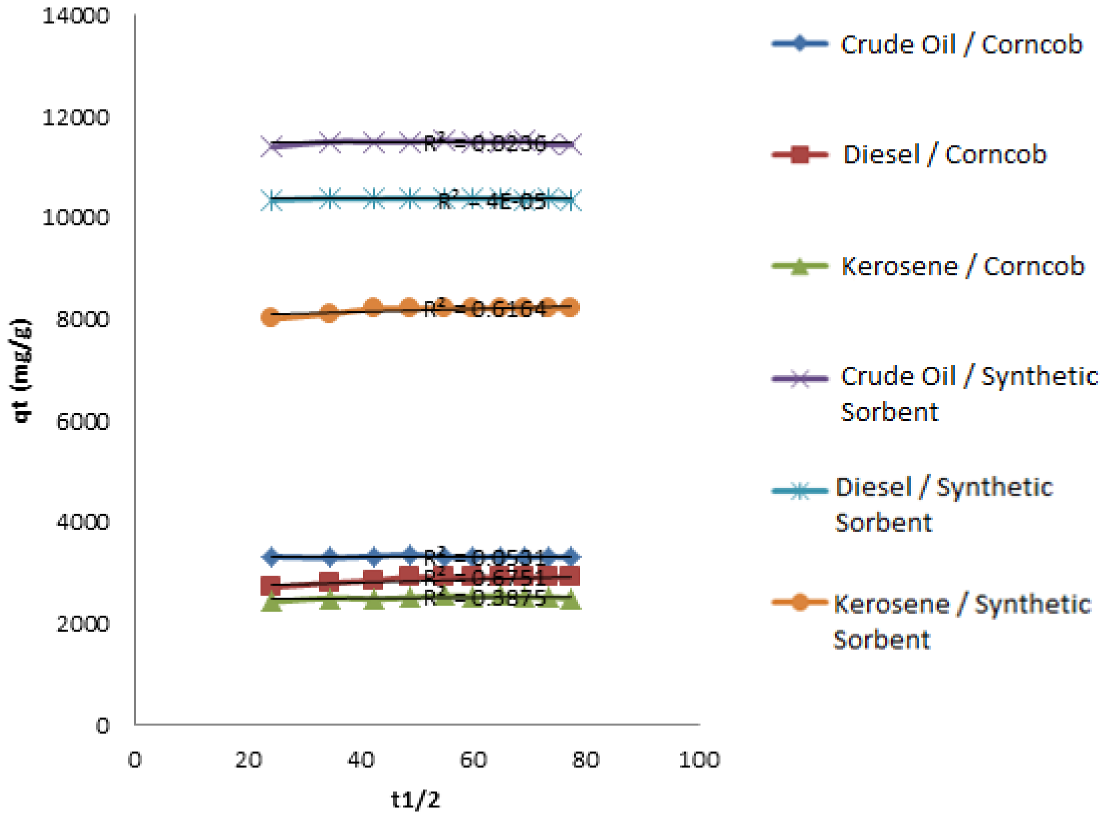

Figure 8: Intraparticle diffusion model $q_t$versus $t^{1}/_{2}$ of sorption of crude oil, diesel and kerosene onto corncob/synthetic sorbent.

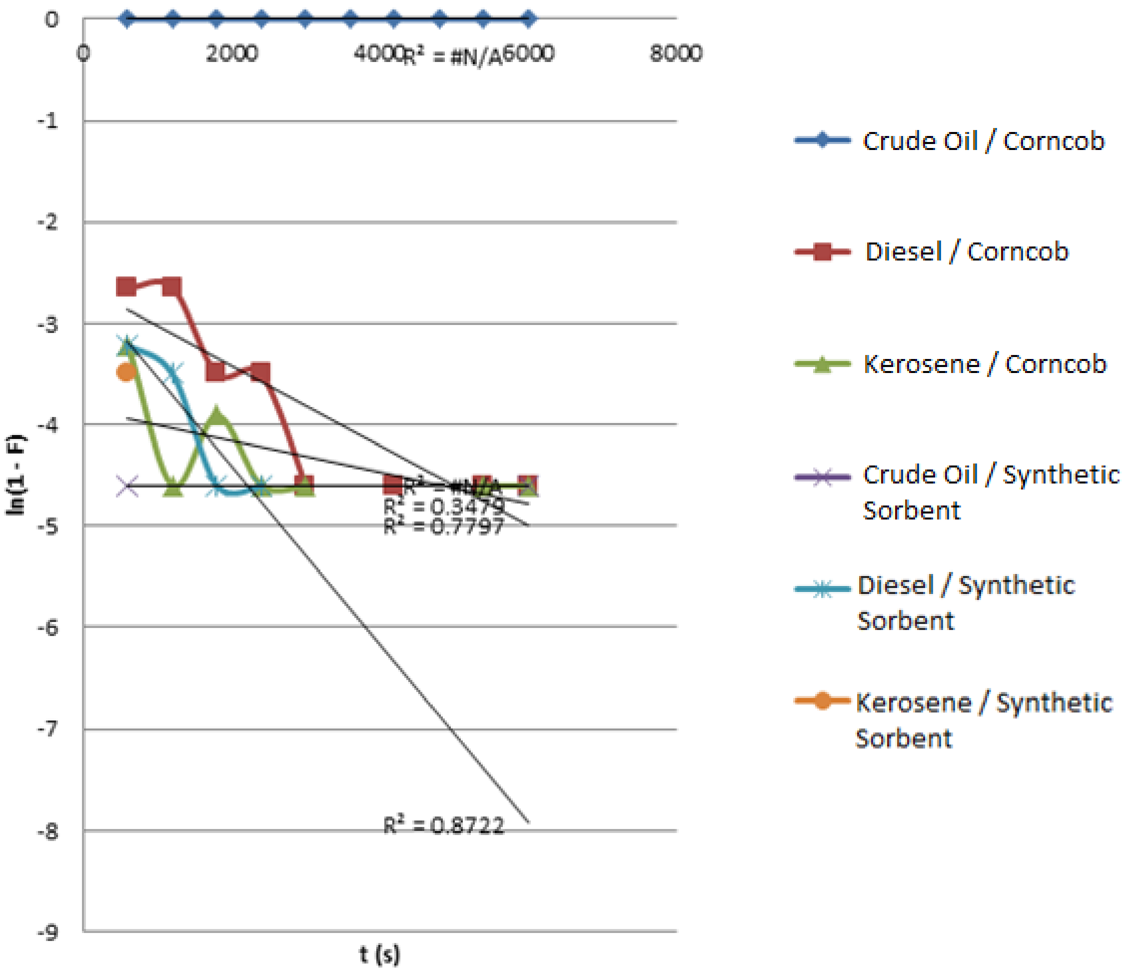

Figure 9: Liquid film diffusion model ln (1-F) versus tof sorption of crude oil, diesel and kerosene onto corncob/synthetic sorbent.

Figs. 8 and 9 show the graphs for both intraparticle diffusion and liquid film diffusion models.

The amount of water sorbed together with each sorbate onto corncob and synthetic sorbentin the experiment to determine suitable environment applicability of corncob and the standard was 17 ml (3.1g) for corncob and 6 ml (1.2 g) for the standard.

DISCUSSION

The result presented in fig. 1 shows that the synthetic sorbent sorbed more oils than corncob, indicating that it has higher oil sorption capacity than corncob. There are several factors which account for sorption, and these include high surface area and highly reactive sorbates and sorbents; organic sorbates chemically bond to the sorbent, if the sorbate and sorbent have mutually reactive moieties (Brown, 1983). Different type of attractive forces between the sorbate and sorbent results in sorption, the extent of these intermolecular attractions depends on molecular chain length and on surface area available for interaction (Weber *et al.*, 1991). Corncobs are lignocellulosic material composed of cellulose, hemicellulose and lignin (Pionter *et al.*,2014). Cellulose consists of subunits of D-pyran glucose with β-1,4-

glucosidicbonds between the subunits, hemicellulose consist of subunits of D-Xylose, mannose, L-arabinose, galactose and glucuronic acid, while lignin consist of subunits of guaiacylpropane, syringyl propane and hydroxylphenylpropane with various ether bonds and carbon – carbon, mainly β-O-4 ether bond between the subunits (Santos Cabral *et al.*, 2016; Chen, 2014). The synthetic sorbent and the sorbates are composed mainly of hydrocarbons; in orderwords, they have mutual reactive moieties than corncob with the sorbates,hence will interact better than with corncob. This in part explains higher oil-sorption capacity of the synthetic sorbent compared to that of corncob. The time during which the sorbents attained sorption equilibrium in each of the sorbates indicates that the standard (40 minutes) attained equilibrium at an earlier time compared with corncob (90 minutes). This may be attributed to the standard having large internal surface area and wide pore volume distribution which enabled faster oil uptake by the standard. The sorption of the sorbates onto corncob and the synthetic sorbent increased as the sorption time increased until equilibrium was attained because three consecutive mass transport steps are associated with the sorption of a solute from solution by a porous sorbent (Faust and Aly 1983). First, the solute migrates through the solution to the external surface of the sorbent particles by molecular diffusion (film diffusion), followed by solute movement from particle surface to interior sites (pore diffusion) and finally the solute absorbed onto these sites, this makes the sorption gradual. Result also indicates that sorption capacity in both corncob and the standard increased with increase in viscosity of the sorbates. Viscosity increases as chain length increases. As chain length increases in a hydrocarbon, its surface area increases. This gives rise to increased intermolecular attraction. As intermolecular attraction increases, sorption increases.

Fig. 3 indicates that the sorption process follows the Langmuir isotherm, which implies that the interaction of both sorbents with the sorbates is monolayer adsorption, that is, one sorbate molecule is adsorbed on a layer of sorbent and there is no interaction between sorbed molecules. Sorbents can be compared by their respective maximum adsorption capacity $q_m$and b values obtained from the Langmuir equation (Volesky, 2004). The maximum adsorption capacity $q_m$is obtained from the isotherm model while q_e is the equilibrium adsorption capacity obtained from experiment (Jing et al, 2010). $q_m$can be interpreted as the total number of binding sites that are available for sorption, and $q_e$as the number of binding sites that are in fact occupied by the sorbate at the equilibrium concentration C_e(Volesky, 2004). The constant b and q_m are obtained from the slope and interception of the plot and are presented in Table 1.The b values obtained for corncob is lower than that obtained for synthetic sorbent. This implies that the synthetic sorbent has greater affinity for the sorbates than corncob. Table 1 shows that the calculated maximum adsorption capacity value (q_m) of corncob andthe synthetic sorbentare slightly higher than their experimental equilibrium sorption capacity value. This further show that Langmuir isotherm provides better fit to the experimental values and can be used to verify the adsorption of crude oil, diesel and kerosene onto corncob and synthetic sorbent. The higher q_m values of synthetic sorbent compared with that of corncob suggest that synthetic sorbent has higher total number of binding sites than corncob, which implies that the synthetic sorbenthas a larger surface area than corncob. This explains why synthetic sorbent sorbed more oil than corncob. The q_m and b values of corncob and synthetic sorbent shows that the synthetic sorbent is a better sorbent than corncob, since a good sorbent would feature a high sorption uptake capacity and high affinity between the sorbent and sorbate (Volesky, 2004).

More of the sorbed oils were recovered from the standard than corncob; this shows that the standard has higher sorbed oil recoverability than corncob, which may be attributed to the standard been composed of porous structure of large internal surface area and wide pore volume distribution,therefore more sorbates diffuse into the pores and effuse easily than in corncob. The percentage value of sorbates retained by the sorbents reveals that corncob retained more of the sorbed oils than the synthetic sorbent; this indicates that it has higher sorbed oil retention than the standard. This attribute makes corncob a suitable sorbent for oil spill removal especially when sorbed oil recovery is not needed. This seems reasonable because one of the key aspects of the overall performance of a sorbent is its ability to retain oil. Some materials rapidly sorb oil but, unless retrieved in good time, the sorbent may subsequently release much of it as a result of effects of wind, waves and currents of the sea. Similarly, some sorbents release oil when lifted from the water as the weight of recovered liquid can cause the sorbent to sag and deform, squeezing oil within pores or internal surfaces (ITOPF Technical Information Paper, 2014; USEPA, 2016), but, in this case, despite subjecting corncob to pressing, it still retained high percentage of the oil it sorbed.

The result of kinetic studies of the rate and mechanism of sorption of crude oil, diesel and kerosene onto corncob and synthetic sorbent presented in Table 1 suggests that the sorption of crude oil, diesel and kerosene onto corncob and synthetic sorbent is not a first order reaction; for sorption of the sorbates onto corncob, the pseudo first order kinetic model correlation coefficients (R^2) value is low. However, it is higher for synthetic sorbent. Moreover, the calculated equilibrium sorption capacities of both sorbents are lower than the experimental values.This implies that the sorption of crude oil, diesel and kerosene onto corncob and the synthetic sorbent is not a first order reaction.

Pseudo second order kinetic model correlation coefficient (R^2) (0.999 – 1.00) and calculated equilibrium adsorption capacities (q_e calc) values of the sorption of the sorbates onto corncob and synthetic sorbent indicate that sorption of the sorbates onto the sorbents fits pseudo-second order kinetics. $q_{e\ calc}$ of each oil onto the sorbents is higher than the experimental values (Table 1), showing the fit of pseudo- second order mechanism for the sorption of crude oil, diesel and kerosene onto corncob and synthetic sorbent. This implies chemisorptions took place during the sorption process, suggesting that when the oils get to the surface of the sorbents due to the driving force obtained from the high concentration of the oils, it encounters fewer active sites or functional groups on the surface to be adsorbed. The high concentration of the oils on the surface then pushes the adsorbed oils from the surface through the pores (intraparticle diffusion) to the internal sites of the sorption. This implies that the sorption process is more likely to conform to intraparticle diffusion mechanism.

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Intraparticle diffusion is the rate-determining step when the plot is linear and passes through the origin (Dawodu and Akpomie, 2014). The plots produced non-zero intercepts (Fig 8.) in both sorbents, suggesting that intraparticle diffusion is not the rate determining step. The deviation from the origin is due to the difference in mass transfer between the initial and final stages of the sorption process (Das and Mondal, 2011). The intraparticle diffusion model regression coefficient (R^2) obtained for the sorption of the sorbates onto corncob and the synthetic sorbent (Fig. 8) are low respectively.This implies that intraparticle diffusion mechanism was not the rate determining step, but was part of the rate determining step of the sorption process in both sorbents.

Plot of $\ln(1-F)$ as a function of t with a zero intercept suggest that the kinetics of a sorption process are controlled by diffusion through the liquid film surface surrounding solid sorbent (Nwadiogbu et al, 2016). Non-zero intercepts were obtained for both corncob and synthetic sorbent (Fig. 9) suggesting that diffusion through the liquid film surface surrounding solid sorbent is not the rate determining step. Liquid film regression coefficients (R^2) values of corncob and the synthetic sorbent are moderate for both corncob and standard (Fig. 9), indicating that surface sorption is not the rate determining step of the sorption process of crude oil, diesel and kerosene onto corncob and synthetic sorbent, but, was part of the rate determining step.

More water was sorbed by corncob as it sorbed oil displaced on water compared with the standard., However the amount of water sorbed is minimal, indicating that corncob could be employed to mop oil spill on water, but once saturated with oil shouldbe removed from the aqueous environment.

In conclusion, corncob has less oil sorption capacity and sorbed oil recoverability, but higher sorbed oil retention than synthetic sorbent. The sorption of crude oil, diesel and kerosene onto corncob is by Langmuir adsorption model. Intraparticle diffusion model and liquid film diffusion model were parts of the rate determining steps of the sorption process of the sorbates onto corncob. Corncob can be applied on land and aqueous environment in oil spill clean-up, but once saturated with oil should be removed from the aqueous environment. Comparatively, corncob is not a very effective oil spill sorbent, but can be useful when oil recovery is not required after oil spill clean-up exercise.

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