EVALUATION OF COCONUT HUSK SORBENT FOR CLEANUP OF PETROLEUM CONTAMINATED ENVIRONMENTS.

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ABSTRACT
In this study coconut husk was tested for removal of crude oil, diesel and kerosene from land and aqueous medium. Oil sorption capacity, recovery of sorbed oil and retain ability of sorbed oil by coconut husk was evaluated and compared with that of a conventional synthetic sorbent used in the oil industry for oil spill clean-up. The experiment was conducted by batch sorption method. The result of the study shows that the conventional synthetic sorbent has higher oil sorption capacity and sorbed oil recoverability than coconut husk, while coconut husk retained more of the sorbed oils. Coconut husk sorbed per unit mass 4.03 ±0.11 g of crude oil, 3.60 ±0.63g of diesel and 2.85 ±0.44g of kerosene while the synthetic sorbent sorbed 11.50 ±0.54g of crude oil, 10.35 ±0.77g of diesel and 8.20 ±0.93g of kerosene. 9.67 ±0.36g of crude oil, 8.40 ±0.95g of diesel and 6.50 ±0.49g of kerosene were recovered from a unit mass of the synthetic sorbent while 3.00 ±0.21g of crude oil, 2.55 ±0.83g of diesel and 2.00 ±0.71g of kerosene were recovered from a unit mass of coconut husk. 1.05 g of crude oil (26 % of sorbed crude oil), 1.05 g of diesel (29 % of sorbed diesel), and 0.80 g of kerosene (28 % of sorbed kerosene) were retained by coconut husk, while, 1.83 g of crude oil (15 % of sorbed crude oil), 1.94 g of diesel (19 % of sorbed diesel) and 1.70 g of kerosene (20 % of sorbed kerosene) were retained by synthetic sorbent. Langmuir adsorption model and pseudo second order models fitted the sorption process more precisely. Intraparticle diffusion mechanism and liquid film diffusion mechanism were part of the rate determining step of the sorption mechanism of the oils onto both sorbents. The synthetic sorbent and coconut husk can be applied on oil spill clean-up on land and surface waters. Coconut husk is not a very efficient sorbent for oil spill clean-up, but can be employed in oil spill clean-up because of its oil retain ability especially when oil recovery is not required but disposal after oil spill clean-up.

Keywords: Coconut husk, adsorption isotherm, adsorption kinetics, crude oil, diesel.

INTRODUCTION
Oil spill is a phenomenon that happens from time to time and is difficult to exclude from petroleum activities because of petroleum exploitation, exploration, movement of crude oil from place to place, oil installation failure [1]. Its consequences on the environment are detrimental because of the environmental degradation it causes and effect on things of value in the environment. For this reason efforts are made to clean up oil when it spills. There are various methods and means of cleaning oil spill in the environment amongst which is the use of sorbents. Sorbents are insoluble materials or mixture of materials used to recover liquids through the mechanism of absorption, or adsorption, or both, and they can be natural or synthetic [2]. Natural materials are cheap, relatively in abundance, renewable and biodegradable.

Oil spill clean-up is a costly exercise, the waste generated after a clean-up exercise using synthetic sorbent needs to be managed through landfill or incineration. This adds to the cost of the clean-up. To abate these problems various studies have been conducted on the viability of natural materials as oil spill sorbent because of their low cost and biodegradability [3]. There is therefore the need to develop low cost and readily available
sorbents, which are biodegradable such that at the end of a clean-up exercise with these sorbents, the oil saturated sorbent is sent to a safe location where it can be biodegraded. Coconut trees are grown in tropical countries mainly for the high oil content of the endosperm which is widely used in both food and non-food industries (e.g. margarine and soaps) [4]. The coconut husks are routinely disposed of after the coconut endosperm and coconut water is sold, this generates waste [5]. The waste generated can be recycled by turning it into a useful product such as sorbent for oil spill. The assessment or performance of sorbing materials often needs to be compared [6]. This helps in efficient application of sorbents. Efficient application of sorbents requires knowledge of data on the sorbent sorption capacity and a good understanding on the basic mechanism behind the sorption capabilities [7]. In order for the comparison of two or more sorbents to be fair, it must be done under the same experimental conditions. By performance of the sorbent is usually meant its uptake (q) of a sorbate [6]. The sorbents can be compared by their respective maximum equilibrium adsorption capacity $q_m$ values which are calculated. A good sorbent would feature a high $q_m$. Also desirable is a high affinity between the sorbent and sorbate [6].

In this study, under the same experimental condition, oil sorption capacity, recovery of sorbed oil and retention of sorbed oil, as well as environment applicability of coconut husk as an oil spill sorbent was determined both on the oils used in this study only and on the oils displaced on water and compared with that of a standard; conventional synthetic sorbent used in the oil industry to clean oil spill, so as to establish its efficiency as an oil spill sorbent and suitable environment applicability of coconut husk sorbent.

**MATERIALS AND METHODS**

**Sample Collection**

Coconut husk was obtained as waste material from a coconut plantation located in Asaba, Delta State, Nigeria. Crude oil and synthetic sorbent mat used as standard in the study were obtained from Shell Petroleum Development Company, Warri, Delta State, Nigeria and Department of Oil Spill Remediation, Shell Petroleum Development Company, Port Harcourt, Rivers State, Nigeria respectively. Diesel and kerosene were purchased from Total filling station located in Asaba, Delta state Nigeria.

**Sample Preparation**

Coconut husk was ground using a mechanical blender and sieved through a sieve of 500 μm (35 mesh) and packaged in pre-cleaned containers. The conventional synthetic sorbent which was in the form of a mat formed a hard mass when blended; it was therefore used as obtained.

**Analysis of Sample**

**Determination of Equilibrium Sorption Capacity and Equilibration Time of Sorption of Crude Oil, Diesel and Kerosene onto Coconut Husk and Synthetic Sorbent**

Crude oil, diesel and kerosene measuring 1 dm$^3$ in volume and 801g, 768g and 760g in weight respectively were each put in a pre-cleaned 2 dm$^3$ beaker. Five (5) g of coconut husk/synthetic sorbent was weighed and added into the beaker and left for a required contact time at 28$^o$ C. The contact times used in this study ranged from 10 to 100 minutes, at 10 minutes interval. At the end of each contact time, the content in the beaker was passed through a sieve of 425μm into 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 difference.

The amount of sorbate sorbed onto a unit mass of coconut husk/synthetic sorbent mat was calculated from:

$$q = \frac{\text{Initial weight–Final weight}}{M}$$

$M =$ mass of sorbent in grams (g)

**Determination of Recovery of Sorbed Crude Oil, Diesel and Kerosene from Coconut husk/Synthetic Sorbent.**
The amount of each sorbate recovered from each sorbent was determined by removing the 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 five minutes, at 28 ° C. After pressing, the sorbent was re- weighed; the weight of sorbate recovered was determined by weight difference.

The amount of sorbate recovered per unit mass of the sorbents was determined as in equation 1. The experiment was performed in triplicate, the average and standard deviation were calculated and used.

The amount of the oils retained per unit mass of the sorbents was obtained from the expression:

\[ q = \text{Quantity of oil sorbed per unit mass of sorbent} - \text{Quantity of oil recovered per unit mass of sorbent} \]

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Application of Adsorption Isotherm to Determine the Adsorption Process of Crude Oil, Diesel and Kerosene onto Coconut husk/Synthetic Sorbent.

The adsorption models applied to determine the sorption process of crude oil, diesel and kerosene onto coconut husk/synthetic sorbent are the linearized form of Langmuir, Freundlich, Elovich, Temkin and Dubinin-Radushkevich adsorption models.

The Langmuir equation may be written as:

\[ q_e = \frac{2m b C_e}{1 + b C_e} \]

Where

- \( q_e \) is the amount of solute adsorbed per unit weight of sorbent at equilibrium (mg /g)
- \( C_e \) is the equilibrium concentration of the solute in the bulk solution (mg L \(^{-1}\))
- \( m \) is the maximum adsorption capacity (mg/g)
- \( b \) is the constant related to the energy of adsorption and temperature, and affinity between the sorbent and sorbate [8].

Langmuir isotherm model can be linearized to five different forms, out of which the forms

\[ \frac{1}{q_e} = \frac{1}{b m C_e} + \frac{1}{q_m} (\text{plot } \frac{1}{q_e} \text{ vs } \frac{1}{C_e}) \] and
\[ \frac{1}{q_e} = \frac{1}{q_m C_e} + \frac{1}{q_m b m C_e} (\text{plot } \frac{C_e}{q_e} \text{ vs } C_e) \]

are the most frequently used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution. A plot of \( \frac{C_e}{q_e} \) against \( C_e \) produces a linear graph with slope = \( \frac{1}{q_m} \) and intercept \( \frac{1}{k_{aqm}} \) and a plot of \( \frac{1}{q_e} \) versus \( \frac{1}{C_e} \) gives a linear graph with slope = \( \frac{1}{k_{aqm}} \) and intercept \( \frac{1}{q_m} \). Both linear forms were applied to the experimental data obtained.

The Freundlich equation can be written as:

\[ q_e = K_f C_e^{1/n} \]

\[ K_f \] is a constant indicative of the relative adsorption capacity of the adsorbent mg\(^{1/(1/n)}\) L\(^{1/n}\)g\(^{-1}\) and \( n \) is a constant indicative of the intensity of the adsorption.

The linear model of Freundlich isotherm can be expressed logarithmically as:

\[ \log q_e = \log C_e + \log K_f \]

Or

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]

Both linear forms were applied to the experimental data obtained.

The values of parameters \( K_f \) and \( \frac{1}{n} \) can be determined from the intercept and slope of the plot \( \log q_e \) against \( \log C_e \) or \( \ln q_e \) against \( \ln C_e \) [10, 11, 12].

Temkin isotherm model is given by:

\[ q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \]

where \( K_T \) is the equilibrium binding constant (L mol\(^{-1}\)) corresponding to the maximum binding energy, \( b \) is related to the adsorption heat, \( R \) is the universal gas constant (8.314 J K\(^{-1}\)mol\(^{-1}\)) and \( T \) is the temperature (K). From the linear plot \( q_e \) against \( \ln C_e \) the slope \( \frac{RT}{b} \) and intercept \( (RT \ln K_T) \) can be determined.

Dubinin-Radushkevich isotherm model is represented as:

\[ q_e = q_o \exp(-B_D[RT \ln(1 + 1/C_e)]^2) \]

Where \( q_o \) is the theoretical adsorption capacity (mg/g), \( B_D \) is a constant related to adsorption energy, \( R \) is gas constant (KJ/mol.K), \( T \) is temperature (K).

The linear form of Dubinin-Radushkevich isotherm model is given as:

\[ \ln q_e = \ln q_o - 2B_D RT \ln(1 + 1/C_e) \]
The plot of $ln q_e$ against $RTln(1 + 1/C_e)$ yields a straight line, the values of $q_D$ and $B_D$ can be calculated from the intercept and slope.

The equation defining the Elovich model is expressed by the equation:

$$\frac{q_e}{q_m} = K_E C_E \exp\left(\frac{q_e}{q_m}\right)$$

where $K_E$ is the Elovich equilibrium constant (L mg^{-1}) and $q_m$ is the Elovich maximum adsorption capacity (mg^{-1}). If the adsorption obeys Elovich equation, Elovich maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the linear plot $\ln \left(\frac{q_e}{C_e}\right)$ versus $q_e$.

Usually to obtain experimental data to be fitted into an adsorption model, different initial concentrations of the sorbate and/or different mass of the sorbent is used during the experiment, so as to produce other values of equilibrium adsorption capacity ($q_e$) and equilibrium concentration ($C_e$) at the end of the experiment.

Five different initial concentrations of crude oil, diesel and kerosene were used to obtain different values of equilibrium adsorption capacity ($q_e$) and equilibrium concentration ($C_e$). The experiment was conducted as mentioned above. The sorbate – sorbent system was left to contact for 80 minutes. The experiment was conducted in triplicate for each initial concentration and the average taken.

**Kinetic Studies**

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

The linearized pseudo-first-order kinetic model, which is also known as the Lagergren equation, can be expressed as:

$$\ln(q_e - q_t) = -k_1 t$$

where $q_t$ and $q_e$ are the amounts of sorbate sorbed at time $t$ (s) and equilibrium, respectively, in mg/g; $k_1$ is the pseudo-first-order rate constant (s^{-1}) [15].

The slope and intercept of the plots of $\ln(q_e - q_t)$ as a function of $t$ were used to determine the rate constant and $q_e$.

The linear form of pseudo – second order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_m^2} + \frac{t}{q_m}$$

Where $k_2$ is the rate constant of the pseudo-second-order expression (g/mg s^{-1}). The $q_e$ and $k_2$ values were calculated from the slope and intercept of the linear plot of $t/q_t$ as a function of the time ($t$) [16].

The initial sorption rate $h$(mg/g s^{-1}) was calculated from the following equation:

$$h = K_2q_e^2$$

The intraparticle diffusion model can be expressed as:

$$q_t = k_d t^{1/2} + I$$

where $q_t$ is the amount of solute sorbed at time $t$, $k_d$ is the intraparticle diffusion rate constant (mg/g s^{1/2}) and $I$ is the intercept. Plot of $q_t$ as a function of $t^{1/2}$ is linear if intraparticle diffusion occurs. The $k_d$ constant is obtained from the slope of the plot of $q_t$ as a function of $t^{1/2}$[17].

The equation representing liquid film diffusion kinetics can be expressed as:

$$\ln(1-F) = -k_{fd} t \ln(1-F) = -k_{fd} t$$

where $F$ is the fractional attainment of equilibrium ($F = q_t/q_e$) and $k_{fd}$ is the rate constant (meq g^{-1} s^{-1/2}) [18]. A plot of $\ln(1 - F)$ as a function of $t$ is linear.

**Determination of Sorption of Crude Oil, Diesel and Kerosene Displaced on Water onto Coconut Husk and Synthetic Sorbent.**

To ascertain the mapping behaviour of coconut husk and synthetic sorbent when the oils are spilled on water, the experiment was repeated with crude oil, diesel and kerosene displaced on water. This was done by pouring 1 (one) dm³ of water into a pre-cleaned 2 dm³ beaker, oil measuring in volume 0.5 dm³ whose initial weight (398g of crude oil, 385g of diesel and 375g of kerosene) had been predetermined was added into the water in the beaker. Five grams of coconut husk/synthetic sorbent was weighed and added into the oil.

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. The sample was ground into fine powder and spread uniformly in between two NaCl based cells. The cells were fixed into the machine and an incident ray of light passed through it. The FTIR spectrophotometer was operated under the following conditions; interferometer: Michelson type with 30° incident angle, dynamic alignment, sealed desiccated, optical system: single beam optics, beam splitter: germanium-coated HBr plate, light source: high brightness ceramic, detector: temperature controlled high sensitivity detector (DLATGS detector), S/N ratio: greater than 20,000: 1 (KRS-5 window), 4CM⁻¹, 1 minute, 2200 CM⁻¹, P-P, wave number: 7,800 CM⁻¹-350 CM⁻¹, resolution: 0.85, 1, 2, 4, 8, 16 CM⁻¹, mirror speed: 3 steps; 2.8, 5, 9 mm/sec, data sampling: He-Ne laser, sample compartment: W200 mm x D230 mm X H170 mm, temperature: 15-30°, relative humidity: less than 70%.

RESULTS AND DISCUSSION

The quantity of crude oil, diesel and kerosene sorbed onto coconut husk and the synthetic sorbent is presented in Fig 1. The equilibrium sorption capacity of coconut husk is 4.03 ±0.11 g of crude oil at 70 min, 3.60 ±0.63 g of diesel at 70 min and 2.85 ±0.44 g of kerosene at 70 min. The equilibrium sorption capacity of the synthetic sorbent is 11.50 ±0.54 g of crude oil at 40 min, 10.35 ±0.77 g of diesel at 60 min and 8.20 ±0.93 g of kerosene at 40 min. The result shows that the synthetic sorbent sorbed more of the oils than coconut husk. Several factors contribute to 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 [19]. Variety of different types of attractive forces between the sorbate and sorbent results in sorption and the extent of these intermolecular attractions depends on molecular chain length and on surface area available for interaction [20]. Coconut husk contains cellulose, hemicellulose and lignin; cellulose consists of subunits of D-pyran glucose with β-1, 4-glicosidic bonds 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 hydroxyphenylpropane with various ether bonds and carbon – carbon, mainly β-O-4 ether bond between the subunits [21, 22]. FTIR spectrum of the synthetic sorbent mat is shown in Fig. 2. The prominent peaks indicates that it is a polyhydrocarbon; 829.42 CM⁻¹ (s) C-H of alkene, 983.73 CM⁻¹ (s) C-H of alkene, 1159.26 CM⁻¹, (s) C-C of alkane, 1369.50 CM⁻¹ (s) C-H of alkane, 1453.41 CM⁻¹(s) C-H of alkane, 2925.15 CM⁻¹(s) C-H of alkane. The synthetic sorbent and the sorbates are composed mainly of hydrocarbons, in other words they have mutual reactive moieties; hence will interact better than with coconut husk. This explains partly why the higher sorption capacity of the synthetic sorbent mat.
Effect of contact time on sorption of crude oil, diesel and kerosene onto coconut husk and synthetic sorbent

The time at which the sorbents attained sorption equilibrium in each of the sorbates indicates that the standard (40 min) attained equilibrium at a shorter time compared with coconut husk (70 min). 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 coconut husk 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 [23]. 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 of both sorbents increases with increase in viscosity of the sorbates as well as chain length.

**Adsorption isotherm studies**

The linearized form \( \frac{C_e}{q_e} \) versus \( C_e \) of the Langmuir adsorption isotherm produced the best fit isotherm (0.99) for the sorption of the sorbates onto the sorbents among the adsorption isotherms applied to the experimental data to describe the adsorption process; Fig. 3 shows the best fit values. This indicates that the adsorption 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 adsorbent and there is no interaction between adsorbed molecules.

![Figure 3: Langmuir Ce/qe versus Ce of sorption of crude oil, diesel and kerosene onto coconut husk/synthetic sorbent](image)

Sorbents can be compared by their respective maximum adsorption capacity \( q_m \) and b values obtained from the Langmuir equation [6]. The maximum adsorption capacity \( q_m \) is obtained from the isotherm model while \( q_e \) is the equilibrium adsorption capacity obtained from experiment [24]. \( q_m \) 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 \( C_e \) [6]. 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 for both coconut husk and synthetic sorbent are 1.00. This implies that both sorbents have same affinity and high affinity for crude oil, diesel and kerosene.

Table 1 show that the calculated maximum
adsorption capacity value ($q_m$) of coconut husk and synthetic sorbent mat are slightly higher than their experimental equilibrium adsorption 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 coconut husk and synthetic sorbent. The higher $q_m$ values of synthetic sorbent for the sorbates compared with those of coconut husk indicates that synthetic sorbent mat has more total number of binding sites than the coconut husk, which implies that, the synthetic sorbent mat has a larger surface area than coconut husk. This contributed to higher oil sorption than coconut husk. The $q_m$ shows that the synthetic sorbent is a better sorbent than coconut husk.

Table 1: Parameters of Langmuir isotherm ($C_e/q_e$ vs $C_e$) and equilibrium sorption capacity ($q_e$) of crude oil, diesel and kerosene onto coconut husk and synthetic sorbent.

<table>
<thead>
<tr>
<th>Sorption type</th>
<th>b (L g$^{-1}$)</th>
<th>$q_m$ (g g$^{-1}$)</th>
<th>$r^2$</th>
<th>$q_e$ (g g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption of crude onto coconut husk</td>
<td>1.00</td>
<td>4.16</td>
<td>0.9956</td>
<td>4.03 ±0.11</td>
</tr>
<tr>
<td>Sorption of diesel onto coconut husk</td>
<td>1.00</td>
<td>3.70</td>
<td>0.9961</td>
<td>3.60 ±0.63</td>
</tr>
<tr>
<td>Sorption of kerosene onto coconut husk</td>
<td>1.00</td>
<td>2.94</td>
<td>0.9947</td>
<td>2.85 ±0.44</td>
</tr>
<tr>
<td>Sorption of crude oil onto synthetic sorbent</td>
<td>1.00</td>
<td>11.62</td>
<td>0.9977</td>
<td>11.50 ±0.54</td>
</tr>
<tr>
<td>Sorption of diesel onto synthetic sorbent</td>
<td>1.00</td>
<td>10.52</td>
<td>0.9979</td>
<td>10.35 ±0.77</td>
</tr>
<tr>
<td>Sorption of kerosene onto synthetic sorbent</td>
<td>1.00</td>
<td>8.40</td>
<td>0.9971</td>
<td>8.20 ±0.93</td>
</tr>
</tbody>
</table>

**Oil recovery and retention characteristics**

Presented in Fig.4 and 5 is the quantity of oils recovered from and retained by synthetic sorbent mat and coconut husk. About 9.67 ±0.36 g of crude oil, 8.40 ±0.95g of diesel and 6.50 ±0.49g of kerosene were recovered from a unit mass of synthetic sorbent while 3.00 ±0.21g of crude oil, 2.55 ±0.83g of diesel and 2.00 ±0.71g of kerosene were recovered from a unit mass of coconut husk. More of the sorbed oils were recovered from the synthetic sorbent than coconut husk, which may be attributed to the synthetic 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 coconut husk. The amount of oils retained by coconut husk is about 1.05g of crude oil (26 % of sorbed crude oil), 1.05g of diesel (29 % of sorbed diesel), and 0.80g of kerosene (28 % of sorbed kerosene), while, 1.83g of crude oil (15 % of sorbed crude oil), 1.94g of diesel (19 % of sorbed diesel) and 1.70g of kerosene (20 % of sorbed kerosene) were retained by synthetic sorbent. Examination of these values reveals that coconut husk retained more of the sorbed oils than the synthetic sorbent mat, this indicates that it is suitable for removal of the sorbates; since one of the features of a good sorbent is high degree of oil retention [6, 25], especially when clean-up does not require recovery but disposal, because 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 [26], but, in this case of coconut husk, despite subjecting it to pressing, it still retained great percentage of the oil it sorbed.

Figure 4: Amount of crude oil, diesel and kerosene recovered from a unit mass of coconut husk/synthetic sorbent.
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 sorption of crude oil, diesel and kerosene onto coconut husk and synthetic sorbent. The result of the pseudo-first-order kinetic model is presented in Table 2; this shows the correlation coefficients ($R^2$) values and the calculated equilibrium adsorption capacities ($q_e$ calc) for the sorption of the oils onto coconut husk and synthetic sorbent. The correlation coefficient ($R^2$) values are low except for sorption of kerosene onto synthetic sorbent mat; moreover the calculated equilibrium adsorption capacities are lower than the experimental values this implies that the sorption of crude oil, diesel and kerosene onto coconut husk and the synthetic sorbent is not a first order reaction.

The pseudo – second order kinetic model correlation coefficient ($R^2$), the calculated equilibrium adsorption capacities ($q_e$ calc) values of the sorption of the oils onto coconut husk and synthetic sorbent are presented in Table 3, the $R^2$ values are 0.999 indicating that adsorption of the oils onto the sorbents fits pseudo-second order kinetics. $q_e$ calc of each oil onto the sorbents is higher than the experimental values, showing the fit of pseudo- second order mechanism for the sorption of crude oil, diesel and kerosene onto coconut husk and synthetic sorbent. This implies chemisorptions took place during the adsorption process. This indicates 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 adsorption. This implies that the adsorption process is more likely to conform to intraparticle diffusion mechanism.

The values of the intercepts of the intraparticle diffusion model are presented in Table 4. When the intercept is larger, surface sorption contributes more to the rate-determining step [27]; the values are low indicating that surface sorption did not contribute more to the rate-determining step. The $k_d$ constant was obtained from the slope of the plot of $q_i$ as a function of $t^{1/2}$. Intraparticle diffusion is the rate-determining step when the plot is linear and passes through the origin [13]. The plots produced non-zero intercepts in both sorbents, suggesting that intraparticle diffusion is not the
rate determining step. The regression coefficient ($R^2$) obtained for both sorbents are moderate, this implies that both intraparticle diffusion mechanism and surface sorption were parts of the rate determining steps of the sorption process. The deviation from the origin is due to the difference in mass transfer between the initial and final stages of the sorption process [28].

A plot of $\ln(1 - F)$ as a function of $t$ with a zero intercept would suggest that the kinetics of the sorption process are controlled by diffusion through the liquid film surface surrounding solid sorbent. Non-zero intercepts were obtained for both sorbents 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 coconut husk and synthetic sorbent are presented in Table 4; these values are moderate for both coconut husk and synthetic sorbent. The result shows that intraparticle diffusion and liquid film diffusion mechanism were parts of the rate determining steps of the sorption process.

**Environment applicability of crude oil, diesel and kerosene displaced on water, onto coconut husk/synthetic sorbent.**

The amount of water sorbed together with each sorbate onto coconut husk and the synthetic sorbent in the experiment to determine suitable environment applicability of coconut husk and the standard was 8 ml (1.31g) for coconut husk and 6 ml (1.2 g) for the standard. These amounts are minimal for each of the sorbent, indicating that coconut husk can be employed to clean oil spill on water.

Table 2: Pseudo – first order kinetic model (lagergren equation) for the sorption of crude oil, diesel and kerosene onto coconut husk and synthetic sorbent.

<table>
<thead>
<tr>
<th>Oil type</th>
<th>$q_e$ exp (mg/g)</th>
<th>$q_e$, Calc (mg/g)</th>
<th>$K_1$ (S$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil (coconut husk)</td>
<td>4030</td>
<td>40.44</td>
<td>0.0006</td>
<td>0.1936</td>
</tr>
<tr>
<td>Diesel (coconut husk)</td>
<td>3600</td>
<td>1211</td>
<td>0.0015</td>
<td>0.6991</td>
</tr>
<tr>
<td>Kerosene (coconut husk)</td>
<td>2850</td>
<td>200</td>
<td>0.0007</td>
<td>0.6697</td>
</tr>
<tr>
<td>Crude oil (synthetic sorbent)</td>
<td>11500</td>
<td>121.51</td>
<td>-0.0066</td>
<td>0.930</td>
</tr>
<tr>
<td>Diesel (synthetic sorbent)</td>
<td>10350</td>
<td>735.09</td>
<td>-0.0009</td>
<td>0.865</td>
</tr>
<tr>
<td>Kerosene (synthetic sorbent)</td>
<td>8200</td>
<td>365.03</td>
<td>-0.001</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 3: Pseudo – second order kinetic model (lagergren equation) for the sorption of crude oil, diesel and kerosene onto coconut husk and synthetic sorbent.

<table>
<thead>
<tr>
<th>Oil type</th>
<th>$q_e$ exp (mg/g)</th>
<th>$q_e$, Calc (mg/g)</th>
<th>$K_1$ (S$^{-1}$)</th>
<th>$R^2$</th>
<th>h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil (coconut husk)</td>
<td>4030</td>
<td>4210</td>
<td>$6.25 \times 10^8$</td>
<td>0.997</td>
<td>1.00</td>
</tr>
<tr>
<td>Diesel (coconut husk)</td>
<td>10340</td>
<td>3703</td>
<td>$7.8 \times 10^8$</td>
<td>0.999</td>
<td>0.99</td>
</tr>
<tr>
<td>Kerosene (coconut husk)</td>
<td>8200</td>
<td>2915</td>
<td>$1.2 \times 10^7$</td>
<td>0.999</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Table 4: Intraparticle diffusion and liquid film diffusion for the sorption of crude oil, diesel and kerosene onto coconut husk and synthetic sorbent.

<table>
<thead>
<tr>
<th>Oil type</th>
<th>Intraparticle diffuson $K_d$(meq g$^{-1}$ S$^{1/2}$)</th>
<th>Intraparticle diffusion $R^2$</th>
<th>Liquid film diffusion $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil (coconut husk)</td>
<td>0.0013</td>
<td>0.168</td>
<td>0.798</td>
</tr>
<tr>
<td>Diesel (coconut husk)</td>
<td>0.007</td>
<td>0.748</td>
<td>0.848</td>
</tr>
<tr>
<td>Kerosene (coconut husk)</td>
<td>0.002</td>
<td>0.594</td>
<td>0.843</td>
</tr>
<tr>
<td>Crude oil (synthetic sorbent)</td>
<td>8.82</td>
<td>0.898</td>
<td>#N/A</td>
</tr>
<tr>
<td>Diesel (synthetic sorbent)</td>
<td>9.06</td>
<td>0.888</td>
<td>0.752</td>
</tr>
<tr>
<td>Kerosene (synthetic sorbent mat)</td>
<td>9.85</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

**Conclusion**

Coconut husks sorbed less crude oil, diesel and kerosene than the synthetic sorbent (standard). Coconut husk has lesser sorbed oil recoverability than the standard and higher oil retain ability than the standard. The adsorption process of the oils onto coconut husk is by Langmuir model and pseudo second order mechanism. Intraparticle diffusion and liquid film diffusion mechanisms were part of the rate determining step of the sorption process of the oils onto coconut husk. Coconut husk can be applied on oil spill clean-up on land and surface waters. Coconut husk is not a very efficient sorbent for oil spill clean-up, however, due to its retain ability, it can be employed in oil spill clean-up when sorbed oil recovery is not needed but disposal..

**REFERENCES**


fibre to fermentable sugars, Bioresources, 7, 1540-1547.


