Acetylated African Oil Bean Seed Pod For Crude Oil Spill Mop

Amalachukwu Ifeyinwa Obi (ai.obi@unizik.edu.ng)
Nnamdi Azikiwe University
https://orcid.org/0000-0003-1002-9248

Vincent Ishmael Ajiwe
Nnamdi Azikiwe University

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ACETYLATED AFRICAN OIL BEAN SEED POD FOR CRUDE OIL SPILL MOP

Amalachukwu I. Obi* and Vincent I. Ajiwe

*Correspondence: ai.obi@unizik.edu.ng

Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria.

ABSTRACT

Oil spill remediation has continued to be a challenge in the world today. Thus efforts are still been made to develop more efficient oil spill mop up techniques. Natural adsorption with agricultural wastes, which otherwise constitute environmental pollution, has become an attractive technique for oil spill mop. Acetylation using acetic anhydride with iodine catalyst was carried out to improve the hydrophobicity of African oil bean seed pod (AOBSP), which is a lignocellulosic material and as such is naturally hydrophilic. Characterization of the raw and acetylated AOBSP were done using SEM, BET and FTIR analyses. Batch crude oil sorption tests were performed using both the raw and acetylated AOBSP. Isotherm, kinetic and thermodynamic studies were also carried out. FTIR analysis showed evidence of successful acetylation of AOBSP and adsorption of crude oil onto the raw and acetylated AOBSP. SEM and BET analyses showed improvement of the surface properties of AOBSP by the acetylation process. The BET surface area increased from 226.4 m$^2$/g for the raw AOBSP to 310.0 m$^2$/g for the acetylated AOBSP. Oil sorption was found to be by monolayer coverage, with monolayer sorption capacity of 5000mg/g and 12500mg/g for raw and acetylated AOBSP, respectively. The rate-controlling mechanism for the sorption processes was chemisorption. Negative values of $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ were obtained, showing that the sorption processes were feasible, spontaneous and exothermic, with a degree of orderliness at the solid–mixture interface. The results obtained from this study show that both raw and acetylated AOBSP are efficient oil sorbents with potentials for further improvement for oil spill mop.
Keywords: Oil bean seed pod, Acetylation, Oil spill mop

INTRODUCTION

Environmental pollution due to crude oil spillage occurs during the various stages of its extraction, transportation, refining, storage, and use. Up to 100 million gallons of crude oil have been estimated to spill into marine environments each year (Barros et al. 2014). This causes adverse effects on aquatic life, human life, local economies, tourism, as well as leisure activities (Wali et al. 2019). Thus, so many efforts are being made towards the development of a very suitable means of oil spill remediation. Many mechanical, biological, chemical and adsorption technologies are been used for removal of oil spills in aqueous environments. However, natural adsorption method using low cost agricultural materials and wastes is a preferred method because of its simplicity, low cost, effectiveness as well as availability, renewability and biodegradability of the sorbents (Xu et al. 2018). These wastes themselves, as well as their disposal usually constitute environmental concerns (Li et al. 2021). Thus, their conversion into valuable products will aid in providing solution to environmental pollution. The major snag with the use of agricultural materials and wastes in oil spill mop is the hydrophilic nature of the materials (Omer et al. 2020), which is as a result of their high hydroxyl content (Anuzyte and Vaisis, 2018). This can, however, be addressed by modification processes which confer hydrophobic properties to the materials (Thompson et al. 2015). Acetylation is one of the most commonly used modification methods, and it changes the hydrophilic nature of lignocellulosic materials to hydrophobic by replacing some of their hydroxyl (–OH) groups with acetyl groups (–COCH$_3$), which are hydrophobic (Onwuka et al. 2019). Acetylation of various agricultural materials such as corn silk (Asadpour et al., 2015), jute fibre (Teli and Valia 2016), corn cob (Nwadiogbu et al. 2016), cocoa pods and oil palm fruit empty bunch (Onwuka et al. 2018) have been carried out in order to improve their oil sorption capacity.

African oil bean seed pod is a readily available, biodegradable waste obtained from the African oil bean tree (Pentaclethra macrophylla). It usually falls off from the tree after splitting open to expel the
seeds which are highly nutritious and usually consumed as food condiment or snack after fermentation or roasting (Nwosu et al. 2017). The empty dry pods are not useful and usually constitute environmental pollution. Studies have been carried out on its use for production of activated carbon (Aningo et al. 2017) and adsorption of heavy metals (Okwunodulu et al. 2015). However, its acetylation for improvement of crude oil sorption potential has not yet been studied.

METHODS

The crude oil used in this work was collected from Port Harcourt Refinery Rivers State, Nigeria. African oil bean seed pods (AOBSP) were collected from Awka environment in Anambra State, Nigeria. They were thoroughly washed with clean water to remove dust and extraneous materials. Then they were dried under sunlight for 12 hours, and then transferred to an oven at 65°C to dry completely. The dried samples were ground using manual grinding machine and sieved. The particles that passed through size 25 British standard sieves (BSS Sieves) were collected and used for further analyses. Acetic anhydride, iodine and all other chemicals used in this work were obtained from British Drug Houses, Ltd.

Crude oil characterization

The density of the crude oil was determined using the density bottle method as reported by Oloro (2018). The °API gravity was obtained using the formula for API (American Petroleum Institute) gravity as expressed by Al-Dahhan and Mahmood (2019). The viscosity of the crude oil was obtained using an NDJ-85 Digital rotary viscometer at 27°C.

Soxhlet extraction

In order to reduce the influence of fiber extracts on acetylation, soxhlet extraction was carried out on the AOBSP. For this, 10g of the sieved materials were extracted with a mixture of n-hexane and acetone (4:1, v/v) for 5 hours. The extracted samples were dried in a laboratory oven for 16 hours.
Acetylation reaction

Acetylation of AOBSP was carried out under mild conditions using the method reported by Nwabueze et al. (2005) which involved acetylation without solvent. A weighed portion (3g) of the AOBSP was reacted with acetic anhydride (60mL) in the presence of 1% iodine catalyst at 30°C for 1 hour. The acetylated samples were then dried in an oven at 60°C for 16 hours, after which they were cooled and stored for further analysis.

Sorbent characterization

Fourier-Transform Infrared (FTIR) spectra was collected using a Nicolet iS5 spectrometer in the spectral range of 4000-400cm⁻¹ in attenuated total reflection (ATR) mode. This was used to identify the functional groups present in the raw and acetylated AOBSP. The surface morphologies of the raw and acetylated AOBSP were observed using Phenom ProX Scanning Electron Microscope by PhenomWorld Eindhoven, the Netherlands. The surface area, pore volume and size were determined using BET analyzer (Quantachrome NOVA 4200e).

Crude oil adsorption

Crude oil for the sorption test was left in a beaker for 24 hours in open air to release volatile hydrocarbon contents, and thus simulate real oil spill situation. Batch sorption tests were carried out using the method described by Nwadiogbu et al. (2016) by contacting 0.2g each of the raw and acetylated AOBSP with 10g of the weathered crude oil displaced in 100 mL of water at 26°C. After 15mins the sorbents were removed using sieving nets and dried at 60°C for 30minutes, after which they were re-weighed. Oil sorption capacity (g/g) was calculated according to the standard method (ASTM F726-99) as shown in Equation 1.

\[
\text{Oil sorption capacity} = \frac{W_1 - W_0}{W_0}
\]  

(1)
where $W_0$ and $W_1$ are the weight of adsorbent before and after oil adsorption, respectively, and the quantity $W_1 - W_0$ is the amount of crude oil adsorbed in grams. The amount of crude oil adsorbed per unit weight of adsorbent, $q_e$ (mg/g), was calculated using Equation 2.

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where $C_o$ is the initial crude oil concentration (mg/L), $C_e$ is the equilibrium crude oil concentration (mg/L), $m$ is the mass of the adsorbent (g) and $V$ is the volume of the solution (L).

**Kinetic study**

Three well known kinetic models were employed to study the kinetics of the oil adsorption. These are the pseudo first order, pseudo second order and intraparticle diffusion models.

**The pseudo first order kinetic model**

The linearized pseudo first order equation is as shown in Equation 3 (Ho and McKay, 2000).

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where $q_e$ is the amount of adsorbate adsorbed at equilibrium (mg/g), $q_t$ is the amount of adsorbate adsorbed in mg/g at time $t$ (min), and $k_1$ is the pseudo first order reaction rate constant (min$^{-1}$). A plot of $\ln (q_e - q_t)$ versus $t$ gives a straight line graph yielding $k_1$ and $q_e$ from its slope and intercept, respectively.

**The pseudo second order kinetic model**

The linearized pseudo second order equation is as expressed in Equation 4 (Ofomaja and Ho, 2007).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where $q_e$ and $q_t$ are the sorption capacity (mg/g) at equilibrium and at time $t$ (min), respectively, and $k_2$ is the pseudo-second order reaction rate constant (g/mg.min). A plot of $t/q_t$ versus $t$ should give a linear relationship, from which $q_e$ and $k_2$ can be determined from the slope and intercept of the plot, respectively.
Intraparticle diffusion model

The intraparticle diffusion model is expressed in Equation 5 (Idris et al. 2012).

\[ q_t = K_{id} t^{0.5} + C \quad (5) \]

where \( K_{id} \) is the rate constant of intraparticle diffusion (mg/(g·min\(^{0.5}\))), \( t^{0.5} \) is the square root of the time, and C is the intercept.

Isotherm study

Two popular isotherms were used to study the equilibrium of the oil adsorption process. They are Langmuir isotherm and Freundlich isotherm.

Langmuir isotherm

The linearized Langmuir isotherm is expressed in Equation 6 (Santos et al. 2015).

\[ \frac{C_e}{q_e} = \frac{1}{K_Lq_m} + \frac{C_e}{q_m} \quad (6) \]

where \( q_m \) is the maximum monolayer adsorption capacity (mg/g) and \( K_L \) (L/mg) is the Langmuir or equilibrium constant of adsorption which is a measure of affinity of the adsorbate for the adsorbent and is related to the energy of sorption. A plot of \( \frac{C_e}{q_e} \) against \( C_e \) yields a straight line graph whose slope and intercept can be used to determine \( q_m \) and \( K_L \), respectively. A dimensionless constant called the separation factor or equation parameter, \( R_L \), which is expressed in Equation 7 (Gupta et al. 2001) is used to predict the affinity between an adsorbent and adsorbate.

\[ R_L = \frac{1}{1 + K_LC_o} \quad (7) \]

where, \( C_o \) is the initial adsorbate concentration. The value of \( R_L \) indicates the adsorption nature to be unfavorable if \( R_L > 1 \), linear if \( R_L = 1 \), favorable if \( 0 < R_L < 1 \) and irreversible if \( R_L = 0 \).

Freundlich isotherm

The linearized Freundlich equation is expressed in Equation 8 (Shah et al. 2021).
\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  

where, \( K_F \) \([(mg/g)/(mg/L)^{1/n}] \) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent, and \( n \) is a measure of the adsorption intensity showing the heterogeneity of the adsorbent site and the energy of distribution. The values of \( K_F \) and \( n \) are determined from the intercept and slope, respectively, of a linear plot of \( \ln q_e \) as a function of \( \ln C_e \). Values of \( n \) between 1 and 10 indicate favourable adsorption (Karthikeyan et al., 2003).

**Thermodynamic studies**

The standard Gibbs free energy changes for the adsorption processes was determined using van’t Hoff equation as shown in Equation 9 (Li et al. 2009).

\[ \Delta G^o = -RT \ln K_d \]  

where \( \Delta G^o \) is the free energy change (kJ/mol), \( R \) is the universal constant (8.314J/mol.K), \( T \) is the absolute temperature (K), and \( K_d \) is distribution coefficient for the adsorption (cm\(^3\)/g). \( K_d \) was calculated using Equation 10.

\[ K_d = \frac{C_s}{C_e} \]  

where \( C_s \) is the amount of adsorbate adsorbed on the sorbent at equilibrium.

The changes in enthalpy, \( \Delta H^o \) (kJ/mol), and entropy, \( \Delta S^o \) (kJ/mol.K) were calculated using Equation 11 (Babarinde et al. 2016).

\[ \Delta G^o = \Delta H^o - T\Delta S^o \]  

A plot of \( \Delta G^o \) versus \( T \) gives a straight line graph from whose slope and intercept \( \Delta S^o \) and \( \Delta H^o \) are obtained, respectively.

**RESULTS AND DISCUSSION**

The characterizing properties of the crude oil are shown in Table 1.
Table 1: Crude oil characterization

| Parameter         | Value |
|-------------------|-------|
| Density (kg/m³)   | 876   |
| °API gravity      | 25.897|
| Viscosity (mPa.s) | 3.958 |

The crude oil is less dense than water and so floats on water. It belongs to the class of medium crudes since its density is within the range of 870 - 920 kg/m³ (Awadh and Al-Mimar, 2015) and the °API gravity is in the range of 22.3 - 31.1° (Yasin et al. 2013). This implies that the crude oil has a blend of light and heavy oils (Madu and Ugwu, 2017).

Surface Morphology Identification

The SEM images of the raw and acetylated AOBSP are shown in Figures 1 and 2, respectively.

![SEM micrograph of raw AOBSP](image)
Figure 2: SEM micrograph of acetylated AOBSP

Acetylation increased the roughness and folds of the raw AOBSP surface, with formation of hollow structures. Similar observation was made by Asadpour et al. (2015) for the acetylation of corn silk. This change in morphology is due to the removal of weak constituents of hemicelluloses and lignin from the AOBSP structure by the acetylating agent (Mahmoud, 2020). This is desirable since it provides more spaces for the retention of oil in the sorbent, thus improving oil sorption and storage (Yusof et al. 2015).

Surface Area Measurements

The results of surface area, pore volume and pore size of the raw AOBSP are shown in Appendix 1A – 1J while for acetylated AOBSP they are shown in Appendix 2A – 2J. The results are summarized in Table 2. According to the International Union of Pure and Applied Chemistry, pore sizes are classified into three groups, which are micropores (diameter less than 20 Å or 2nm), mesopores (diameter between 20 Å or 2nm and 500 Å or 50nm), and macropores (diameter greater than 500 Å or 50 nm) (Asadpour et al. 2014). The pore size/diameter of the raw and acetylated AOBSP were in the same range and belonged to the mesopore group. Acetylation was found to substantially increase the surface area and pore volume of AOBSP. These increments are likely due to the formation of hollow structures.
and increased roughness and folds of the raw AOBSP surface, as observed in SEM analysis. This is favorable since high active surface area results in high oil adsorption capacity (Angelova et al. 2011).

4.3 Fourier Transform Infra-red spectroscopy (FTIR)

The FTIR spectra for raw and acetylated AOBSP, before and after crude oil sorption, are shown in Figures 3 - 6, respectively. The assignment of functional groups are shown in Table 3.

Figure 3: FTIR spectrum of raw African oil bean seed pod (RAOBSP)

Figure 4: FTIR spectrum of acetylated African oil bean seed pod (AAOBSP)
Figure 5: FTIR spectrum of raw African oil bean seed pod after sorption (RAOBSP-S)

Figure 6: FTIR spectrum of acetylated African oil bean seed pod after sorption (AAOBSP-S)
Table 3: FTIR bands of AOBSP and the corresponding functional groups

|          | RAOBSP (cm\(^{-1}\)) | AAOBSP (cm\(^{-1}\)) | RAOBSP-S (cm\(^{-1}\)) | AAOBSP-S (cm\(^{-1}\)) | Assignment                                      |
|----------|----------------------|-----------------------|-------------------------|-------------------------|------------------------------------------------|
| RAOBSP   | 3368.93              | 3329.43               | 3364.25                 | -                       | O–H stretching in cellulose and hemicellulose    |
| AAOBSP   | -                    | 2901.04               | 2921.28                 | 2921.15                 | C–H stretching of methyl and methylene groups    |
| RAOBSP-S | 2191.56              | 2160.30               | 2852.46                 | 2852.49                 | Cyanide ion stretching                           |
| AAOBSP-S | 1616.34              | 1723.78               | 1629.79                 | 1605.90                 | C=O stretching vibration                         |
|          |                      |                       | 1612.84                 |                         |                                                 |
|          | 1507.58              | 1508.03               | -                       | -                       | C=C stretching of aromatic ring                  |
|          | 1320.06              | 1425.97               | 1456.20                 | 1456.19                 | C–H bending                                      |
|          |                      |                       | 1317.16                 | 1376.12                 |                                                 |
|          |                      |                       | 1376.38                 |                         |                                                 |
|          | 1232.98              | 1232.88               | 1240.88                 | 1032.71                 | C–O stretching vibration                         |
|          | 1029.68              | 1158.60               | 1032.05                 |                         |                                                 |
|          |                      |                       | 1029.09                 |                         |                                                 |
|          | -                    | -                     | 810.05                  | 810.75                  | C–H bending of β glycosidic bond                 |
|          | 548.50               | 534.12                | -                       | 744.63                  | C–H out of plane bending                         |
|          | to                   | to                    |                         |                         |                                                 |
|          | 504.21               | 516.32                |                         |                         |                                                 |

Note: RAOBSP is raw AOBSP; AAOBSP is acetylated AOBSP; RAOBSP-S is raw AOBSP after crude oil sorption; and AAOBSP-S is acetylated AOBSP after crude oil sorption.
A comparison of the spectra of RAOBSP and AAOBSP shows the following major differences: creation of absorption peak at 2901.04 cm\(^{-1}\) (C–H stretching), enhancement of absorption peaks at 1612.84 – 1723.78 cm\(^{-1}\) (C=O stretching) and at 1029 cm\(^{-1}\) (C–O stretching). These show evidence of acetylation of AOBSP (Onwuka et al. 2016). The lack of peaks at 1700 cm\(^{-1}\) (carboxylic group) and in the region of 1760-1840 cm\(^{-1}\) in the spectra of the acetylated sample indicates that the product was free of acetic acid byproduct and unreacted acetic anhydride (Bodîrlău and Teacă, 2009).

The spectra of the crude oil-treated sorbents show the appearance of intense sharp peaks at 2921 cm\(^{-1}\), 2852 cm\(^{-1}\) and 1376.12 – 1456.40 cm\(^{-1}\) which correspond to CH\(_3\), CH\(_2\) and C-H bending of crude oil showing that crude oil was adsorbed to the adsorbents (Kudaybergenov et al. 2013). These peaks are found to be more intense in AAOBSP-S than RAOBSP-S showing that the acetylated sample adsorbed more crude oil than the raw sample. The spectra of AAOBSP-S shows absence of peak at 3329.43 – 3368.93 cm\(^{-1}\) (O–H stretching), as well as reduced peaks at 1029.09 – 1232.98 cm\(^{-1}\) (C–O stretching) and 1605.63 – 1629.79 cm\(^{-1}\) (C=O stretching). This may indicate the involvement of these groups in the adsorption of crude oil to the acetylated sample (Shittu et al. 2020). The obtained FTIR spectra are consistent with those reported for crude oil adsorption by raw and acetylated corn silk (Asadpour et al. 2015) and Delonix regia pods (Onwuka et al. 2016).

**Adsorption Studies**

The effects of different parameters on the crude oil sorption capacity of both the raw and acetylated AOBSP were studied and the results are as follows.

**Effect of contact time**

The effect of contact time on crude oil sorption capacity of the raw and acetylated AOBSP is shown in Figure 7.
The crude oil sorption capacity of the adsorbents was found to increase with increase in contact time from 1 to 15 minutes. The sorption process was rapid at the initial stages of contact and thereafter it became slower towards equilibrium. This may be due to the fact that at the onset of contact, the high concentration gradient between the oil solution and the sorbent surface leads to high diffusion of oil into the pores of the sorbent. But, as time passed, the adsorbed oil started to clog the sorbent’s pores and so oil could no longer diffuse to the active sites deep within the sorbent (Najaa-Syuhada et al. 2017). Similar trend was reported for crude oil adsorption on raw and acetylated *Borassus aethopum* coir by Arinze-Nwosu et al. (2019).

Throughout the adsorption period, the acetylated AOBSP had higher sorption capacity than the raw AOBSP. At 15 minutes of contact time, the sorption capacities of the raw and acetylated AOBSP were 7.430 g/g and 11.795 g/g, respectively. The higher sorption capacity of the acetylated AOBSP is likely due to its higher surface area and pore volume, as observed in surface area analysis, which provides more spaces for oil adsorption. Increase in crude oil sorption capacity on acetylation was also reported by Onwuka et al. (2018) who found the crude oil adsorption capacity of raw and acetylated cocoa pods...
to be 3.97 and 6.65 g/g, respectively, while raw and acetylated oil palm empty fruit bunch had values of 3.04 and 6.48 g/g, respectively.

**Effect of temperature**

The effect of temperature on the crude oil sorption capacity of the raw and acetylated AOBSP is shown in Figure 8.

![Figure 8: Effect of temperature on crude oil adsorption capacity](image)

Crude oil sorption capacity decreased with increase in temperature from 30°C to 50°C. This may be due to the fact that increase in temperature accelerates the Brownian motion of the oil molecules, thus a stronger force is needed to keep the molecules adsorbed to the sorbent surface (Simonivić et al. 2009). The decrease in the crude oil sorption capacity with increasing temperature also shows that the adsorption process was exothermic in nature. Similar behaviour was reported by El-Din et al. (2018) for the use of banana peels to adsorb 1-day and 7-day weathered crude oil. An increase in temperature from 20 to 45°C resulted in decrease of sorption capacity of the sorbent from 7.94 g/g and 7.14 g/g to 4.52 g/g and 3.25 g/g for 1-day and 7-day weathered crude oil, respectively.
Effect of adsorbent dose

The effect of adsorbent dose on the crude oil sorption capacity of the raw and acetylated AOBSP is shown in Figure 9 while the effect of adsorbent dose on the amount of crude oil adsorbed is shown in Figure 10.

**Figure 9: Effect of adsorbent dose on amount of crude oil adsorbed**

**Figure 10: Effect of adsorbent dose on crude oil sorption capacity**
As sorbent dose increased from 0.2g to 1g, amount of crude oil adsorbed on both the raw and acetylated AOBSP increased from 0.734mg/g to 3.113mg/g and 1.869mg/g to 6.860mg/g, respectively. This may be due to the fact that increase in quantity of adsorbent resulted in the availability of more surface area/active binding sites (Akinhanmi et al. 2020). However, as the sorbent dose increased, there was a general decrease in the crude oil sorption capacity of both the raw and acetylated AOBSP. This decrease may be due to the fact that as sorbent dose increases, sorption sites aggregate and overlap, thereby reducing total accessible surface area. This results in reduction of the quantity of sorbate adsorbed by a unit mass of sorbent, which leads to reduction of sorption capacity (Shweta and Jha 2016). Similar behaviour was reported by Nwadiogbu et al. (2016) who found the crude oil sorption capacity of raw and acetylated corn cob to decrease from 4000mg/g to 1000mg/g and 2300mg/g to 500mg/g, respectively on increasing the sorbent dosage from 0.5g to 2g.

**Kinetic study**

The pseudo first order, pseudo second order and intraparticle diffusion data for crude oil adsorption on raw and acetylated AOBSP are shown in Figures 11 – 13.

![Figure 11: Pseudo first order kinetic plot](image_url)
Figure 12: Pseudo second order kinetic plot

Figure 13: Intra particle diffusion kinetic plot

The kinetic parameters are shown in Table 4.
Table 4: Kinetic parameters for oil adsorption on raw and acetylated AOBSP

| Parameter          | RAOBSP  | AAOBSP  |
|--------------------|---------|---------|
| $q_e$, exp (mg/g)  | 7430    | 11795   |

**Pseudo first order model**

- $R^2$: 0.8621, 0.9504
- $k_1$ (min$^{-1}$): 0.0882, 0.2337
- $q_e$, calc. (mg/g): 6281, 9509

**Pseudo second order model**

- $R^2$: 0.8307, 0.9836
- $k_2$ (min$^{-1}$): $1.7 \times 10^{-5}$, $2.5 \times 10^{-5}$
- $q_e$, calc. (mg/g): 10000, 14286

**Intraparticle diffusion model**

- $R^2$: 0.9182, 0.9254
- $K_{id}$ (mg/(g·min$^{0.5}$)): 1774.5, 2257.10
- C: -101.93, 3410.70

All the kinetic plots were found to be linear with high $R^2$ values (0.8307 - 0.9836). The pseudo-first, pseudo-second and intraparticle diffusion rate constants are higher for adsorption on acetylated AOBSP than on raw AOBSP. This suggests that physisorption, chemisorption as well as intraparticle diffusion of the crude oil was faster on acetylated AOBSP than on raw AOBSP, and this can be ascribed to the hydrophobicity of the acetylated AOBSP (Onwuka et al. 2016). The intra particle diffusion model graphs, though linear, did not pass through the origin. This shows that intra-particle diffusion took part in controlling the rate of oil sorption on both RAOBSP and AAOBSP, but it was not the sole mechanism (Thompson et al. 2015). The $K_{id}$ value of AAOBSP was found to be higher than that of RAOBSP.
showing that acetylation improved the adsorptive potential of AOBSP since higher $K_{id}$ values indicate increase in the rate of adsorption as well as better adsorption mechanism (Erhan et al. 2004).

For adsorption on both raw and acetylated AOBSP, the pseudo-second order rate constant is lower than the pseudo-first order rate constant. This shows that chemisorption is the slowest step, and so is the rate-controlling step in the sorption process. This is supported by the fact that for adsorption on acetylated AOBSP, the pseudo-second-order $R^2$ value (0.9836) is higher than the pseudo-first-order $R^2$ value (0.9504). For adsorption on raw AOBSP the pseudo-first-order $R^2$ value (0.8621) is higher than the pseudo-second-order $R^2$ value. However, the pseudo-second-order value (0.8307) is also high and close to the pseudo-first-order value. Thus, it can be said that chemisorption is the rate-controlling mechanism in the sorption of oil on both raw and acetylated AOBSP, with physisorption being partly involved in the sorption process.

4.7.3 Isotherm studies

The Langmuir isotherms for crude oil adsorption on raw and acetylated AOBSP are shown in Figures 14 and 15, respectively, while the Freundlich isotherms are shown in Figures 16 and 17 for adsorption on raw and acetylated AOBSP, respectively.

![Langmuir isotherm for oil adsorption on raw AOBSP](image)

**Figure 14: Langmuir isotherm for oil adsorption on raw AOBSP**

\[ y = 0.0002x + 6.9726 \]

$R^2 = 0.7111$
**Figure 15:** Langmuir isotherm for oil adsorption on acetylated AOBSP

\[ y = 8E-05x + 2.4368 \]
\[ R^2 = 0.8121 \]

**Figure 16:** Freundlich isotherm for oil adsorption on raw AOBSP

\[ y = 0.3215x + 4.5375 \]
\[ R^2 = 0.3161 \]
The isotherm parameters for the crude oil adsorption on raw and acetylated AOBSP are shown in Table 5.

**Table 5: Isotherm parameters for oil adsorption on raw and acetylated AOBSP**

| Parameter      | RAOBSP       | AAOBSP       |
|----------------|--------------|--------------|
| **Langmuir isotherm** |              |              |
| $R^2$           | 0.7111       | 0.8121       |
| $K_L$ (L/mg)   | $2.87 \times 10^{-5}$ | $3.28 \times 10^{-4}$ |
| $R_L$          | 0.26         | 0.23         |
| $q_m$ (mg/g)   | 5000         | 12500        |
| **Freundlich isotherm** |              |              |
| $R^2$           | 0.3161       | 0.5931       |
| $K_F$          | 93.457       | 292.57       |
| $n$            | 3.11         | 3.33         |
For both RAOBSP and AAOBSP the $R^2$ values for Langmuir isotherm are higher than for Freundlich isotherm. This means that the adsorption of crude oil on both RAOBSP and AAOBSP are better described by Langmuir isotherm than Freundlich isotherm. This shows that oil adsorption on both RAOBSP and AAOBSP took place by monolayer coverage of the sorbents by the crude oil with no interaction between the adsorbed oil on adjacent sites (Mwangi et al. 2012). The $K_L$ value for adsorption on AAOBSP ($3.28 \times 10^{-4}$ L/mg) is higher than the value for adsorption on RAOBSP ($2.87 \times 10^{-5}$ L/mg). This shows that there was greater affinity between the crude oil and AAOBSP than between the crude oil and RAOBSP. The $R_I$ values were 0.26 and 0.23 for RAOBSP and AAOBSP, respectively. These values are between 0 and 1, thereby indicating the favourability of the adsorption of crude oil on both sorbents (Siswoyo et al. 2014). The monolayer sorption capacity was found to be 5000 mg/g for RAOBSP and 12500mg/g for AAOBSP, which shows the high improvement of the sorption capacity of AOBSP by acetylation. The sorption capacity of acetylated AOBSP is higher than some other reported acetylated lignocellulosic wastes, such as acetylated groundnut husk with sorption capacity of 9940mg/g (Chiaha et al. 2017) and acetylated oil palm empty fruit bunch fibre with sorption capacity of 10,000mg/g (Asadpour et al. 2016).

**Thermodynamic studies**

The results of thermodynamic analysis of crude oil adsorption on the raw and acetylated AOBSP are shown in Table 6.
Table 6: Thermodynamic parameters for oil adsorption on raw and acetylated AOBSP

| Parameter   | RAOBSP     | AAOBSP     |
|-------------|------------|------------|
| ΔG° (kJ/mol) | -10.120    | -12.031    |
| 303K        | -10.093    | -12.008    |
| 308K        | -9.920     | -11.996    |
| 313K        | -9.148     | -11.426    |
| 318K        | -8.650     | -10.365    |
| ΔH° (kJ/mol) | -33.906    | -36.067    |
| ΔS° (kJ/mol) | -0.0777    | -0.0783    |

For adsorption on both RAOBSP and AAOBSP, ΔG° was found to have negative values at all the considered adsorption temperatures, showing that adsorption on both RAOBSP and AAOBSP were spontaneous and feasible and so did not require any external energy source (Adeogun et al. 2016). Higher negative ΔG° value shows a more energetically favorable adsorption (Kumar 2011). AAOBSP was found to have higher negative ΔG° values than RAOBSP at all the considered adsorption temperatures showing that adsorption of crude oil on AAOBSP was more energetically favorable than adsorption on RAOBSP. Also, lower negative ΔG° values were obtained with increase in temperature, showing that there was more efficient biosorption at lower temperature, which is supported by the decrease in the value of sorption capacity of the sorbents with increase in temperature observed during the study of effect of temperature on adsorption. The ΔH° values were negative values, also confirming that crude oil adsorption on both RAOBSP and AAOBSP were exothermic processes. The ΔS° values were found to be -0.0777kJ/mol and -0.0783kJ/mol for adsorption on RAOBSP and AAOBSP,
respectively. The negative value of $\Delta S^\circ$ shows that there was a reduction in randomness at the solid–mixture interface during adsorption (Salisu et al. 2019). This is as a result of the adsorption of the oil molecules to the sorbents’ surfaces thereby leading to orderliness (Zhu et al. 2009). Also, according to Nwosu et al. (2012), negative $\Delta S^\circ$ values show that the adsorption process did not result in any significant change in the internal structure of the adsorbent. Thus, crude oil adsorption on both raw and acetylated AOBSP was feasible, spontaneous, exothermic, and did not cause any significant change in the internal structure of the adsorbent.

**CONCLUSION**

In this study, AOBSP, which is an agricultural waste, was found to be a suitable sorbent for crude oil removal from aqueous solution. The sorption capacity increased substantially after acetylation. Crude oil adsorption on both raw and acetylated AOBSP were spontaneous, exothermic, and did not cause any significant change in the internal structure of the adsorbents. Adsorption on the raw pod was best described by the pseudo first order kinetic model, while adsorption on the acetylated pod fitted best to the pseudo second order model. Intra-particle diffusion also took part in controlling the rate of oil sorption on both RAOBSP and AAOBSP. Adsorption on both raw and acetylated AOBSP took place by monolayer coverage of the crude oil on the surface of the sorbents with the sorption capacity of the raw and acetylated sorbents being 2500mg/g and 12500mg/g, respectively. Acetylated AOBSP is a very promising alternative sorbent for crude oil spill mop because of its high sorption capacity and the fact that AOBSP is readily available and a biodegradable waste.

**Abbreviations**

AOBSP: African oil bean seed pod; RAOBSP: raw African oil bean seed pod; AOBSP: acetylated African oil bean seed pod; RAOBSP-S: raw African oil bean seed pod after crude oil sorption; AAOBSP-S: acetylated African oil bean seed pod after crude oil sorption; API: American Petroleum
Institute; ATR: attenuated total reflection; ASTM: American Society for Testing and Materials; SEM: Scanning electron microscopy; BET: Brunauer, Emmett and Teller; BJH: Barrett, Joyner, and Halenda; DH: Dollimore and Heal; DR: Dubinin-Radushkevich; DFT: Density functional theory; HK: Horvath and Kawazoe; SF: Saito and Foley; DA: Dubinin-Astakhov; FTIR: Fourier-Transform Infrared; W₀: weight of adsorbent before oil adsorption; W₁: weight of adsorbent after oil adsorption; C₀: initial crude oil concentration (mg/L); Cₑ: equilibrium crude oil concentration (mg/L); m: mass of adsorbent (g); V: volume of solution (L); qₑ: amount of adsorbate adsorbed at equilibrium (mg/g); qₜ: amount of adsorbate adsorbed (mg/g); t: time (min); k₁: pseudo first order reaction rate constant (min⁻¹); k₂: pseudo-second order reaction rate constant (g/mg.min); Kᵢₐ: rate constant of intraparticle diffusion (mg/(g·min⁰.⁵)); Kₐ: Langmuir constant (L/mg); Rₐ: Langmuir separation factor; Cₒ: initial adsorbate concentration(mg/L); Kₐ: Freundlich constant [(mg/g)/(mg/L)⁰.₅ⁿ]; n: measure of adsorption intensity; R: universal constant (8.314J/mol.K); T: absolute temperature (K); Kₐ: distribution coefficient for adsorption (cm³/g); ΔGₒ: standard Gibbs free energy change (kJ/mol); ΔHₒ: change in enthalpy (kJ/mol); ΔSₒ: change in entropy (kJ/mol).

DECLARATIONS

Ethics approval and consent to participate
Not applicable

Consent for publication
Not applicable

Availability of data and materials
All data generated or analysed during this study are included in this published article (and its supplementary information files).
Competing interests

The authors declare that they have no competing interests.

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Authors’ contributions

AIO who is a doctoral candidate wrote the manuscript. VIA is the supervisor and provided comments and revisions to the manuscript. All authors read and approved the final manuscript.

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## Table 2: Surface area measurements of African oil bean seed pod (AOBSP)

| Measurement                                                                 | Raw AOBSP | Acetylated AOBSP |
|----------------------------------------------------------------------------|-----------|------------------|
| **Surface area (m$^2$/g)**                                                 |           |                  |
| SinglePoint BET                                                            | 137.7     | 192.0            |
| MultiPoint BET                                                             | 226.4     | 310.0            |
| Langmuir surface area                                                      | 1358      | 1620             |
| BJH method cumulative adsorption surface area                              | 255.1     | 355.1            |
| DH method cumulative adsorption surface area                               | 271.3     | 378.3            |
| t-method external surface area                                             | 226.4     | 310.0            |
| DR method micropore area                                                  | 242.4     | 335.8            |
| DFT cumulative surface area                                               | 53.93     | 74.76            |
| **Pore volume (cc/g)**                                                    |           |                  |
| BJH method cumulative adsorption pore volume                              | 0.1254    | 0.1741           |
| DH method cumulative adsorption pore volume                                | 0.1283    | 0.1783           |
| DR method micropore volume                                                | 0.0861    | 0.1193           |
| HK method micropore volume                                                | 0.0359    | 0.0505           |
| SF method micropore volume                                                | 0.0074    | 0.0108           |
| DFT method cumulative pore volume                                         | 0.0652    | 0.0895           |
| **Pore size (nm)**                                                        |           |                  |
| BJH method adsorption pore diameter                                        | 2.123     | 2.131            |
| DH method adsorption pore diameter                                         | 2.123     | 2.131            |
| DR method micropore width                                                 | 6.247     | 6.181            |
| DA method pore diameter                                                   | 2.940     | 2.920            |
| Method                      | Value 1 | Value 2 |
|-----------------------------|---------|---------|
| HK method pore diameter     | 1.847   | 1.847   |
| SF method pore diameter     | 3.497   | 3.488   |
| DFT pore diameter           | 2.647   | 2.647   |
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