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RESEARCH ARTICLE

Comparative Evaluation of the Structural and Adsorptive Properties of Modified and Unmodified Cucurbita Moschata Seed Husk for Crude Oil Spill Clean-up

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Abstract: This study investigates the structural and adsorption properties of modified and unmodified *Cucurbita moschata* seed husk with a view to evaluating its potential as a low-cost bio-sorbent for crude oil clean-up. The raw seed husk was subjected to chemical modification through acetylation, aiming to enhance its surface characteristics and functional group availability. Comprehensive characterizations were conducted using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and surface area analysis to determine changes in morphology and functional groups. Batch adsorption experiments were carried out to assess the sorption efficiency of both modified and unmodified *Cucurbita moschata* seed husk in removing crude oil from aqueous solutions under varying conditions of contact time, catalyst usage. Adsorption kinetics and isotherm models, including first-order, pseudo-second-order, Intra diffusion, Freundlich, Langmuir and Temkin were applied to interpret the experimental data. The results revealed that acetylation significantly improved the surface roughness, porosity and active binding sites of the sample, leading to enhanced oil uptake capacity. The modified *Cucurbita moschata* seed husk exhibited superior adsorption efficiency, with equilibrium data fitting well to the Freundlich isotherm and Pseudo-second order kinetic model, indicating multilayer adsorption on a heterogeneous surface. These findings suggest that modified *Cucurbita moschata* seed husk, holds promising potential as a sustainable, ecofriendly, and effective adsorbent for treating oil spill clean-up in our environment.

Keywords: *Cucurbita moschata*, acetylation, kinetics, isotherm, oil spillage

1 Introduction

Crude oil occurs as a dark, sticky, viscous liquid. It is a mixture of gaseous liquid and solid alkanes, alkenes, cycloalkanes, aromatic hydrocarbons and others. It is one of the most precious resource on the earth. and very crucial for the day to day activities of all living creatures. It plays an indispensable role in the world economy. The need for crude oil is continuously increasing with growing population and industrialization in the environment. Crude oil spill is a recent issue of concern for the whole world as oil spill is not accessible in many regions of the world. It is tragic environmental disasters that can cause severe health problems, disturb the ecosystem and pollute the environment. They affect human health through both the chemical exposure and the psychological and socioeconomic impact on the affected individuals and their communities. Despite the considerable number of accidental oil spills that occurred around the world, only very few of them have been studied in terms of their effects on human health [1–3]. Aquatic life human life, local economics, tourism and leisure activities are also affected [4].

Since the industrial revolution of the eighteenth century, the use of fossil fuels specially refined petroleum products have increased exponentially during this process, off-shore oil production using floating drilling rigs and transportation of both crude and refined oil products using supertankers have also increased throughout the world. This has led to number of accidental spills into the sea, posing potential health risk to the marine environment. Although more than 40 oil spill disasters have occurred around the world, attention to their potential health effects has increased lately because of the recent Gulf oil spill in the United States. These oil spill pollute water, air and food because of the release of various toxic chemicals such as volatile hydrocarbons and trace metals. Moreover, these spills are environmentally hazardous causing disease and death [1].

Crude oil spills are tragic environmental disasters that can cause severe health problems, disturb the ecosystem and pollute the environment. They affect human health through both the

chemical exposure and the psychological and socioeconomic impact on the affected individuals and their communities. Despite the considerable number of accidental oil spills that occurred around the world, only very few of them have been studied in terms of their effects on human health [1].

Marine oil spills emanating from wells, pipelines, freighters, tankers, and storage facilities draw public attention and necessitate quick and environmentally friendly response measures. It is sometimes feasible to contain the oil with booms and collect it with skimmers or burn it, but this is impracticable in many circumstances, and all that can be done without causing further environmental damage [5].

Large amounts of agricultural waste (corn cob, corn husk, plantain peel, plantain pseudostem, bread fruit seed husk, *Borassus coir*, etc.) are produced in many homes. However, many of these waste materials are not reused. One of the features of these organic materials is that it can absorb by capillary forces an amount of oil and/or water greater than its own weight [6].

Furthermore, these natural materials can be completely degraded in nature by biological, physical, chemical and photochemical processes [7].

In small scale spills, oil can be removed with a sorbent. The sorbent in use today can be classified as either polymer, natural materials, or treated cellulosic materials [7]. Recently reviewed the porous materials used for spill cleanup, and several studies of different natural, synthetic and mineral sorbents have also been conducted [8]. Most recently used commercial sorbents are synthetic sorbents made of polypropylene and polyurethane [9]. They have good hydrophobic and oleophilic properties, but their non-biodegradability is a major disadvantage [8].

Nwadiogbu (2015) [10] studied the equilibrium and kinetic studies of the removal of crude oil from aqueous medium by sorption on hydrophobic corncobs. They observed that the sorption process occurred via a surface reaction and intra-particle diffusion mechanism. They further reported that the maximum monolayer sorption capacities were 0.0768 mg/g and 0.0043 mg/g for the acetylated and raw corn cobs respectively. Sun et al. (2004) [11] esterified sugar bagasse with acetic anhydride using N-Bromosuccinimide as a catalyst under mild conditions. The acetylation increased hydrophobic properties of the bagasse obtained at 80^{o}C for 6 hours and was found to be 1.9 times better than the commercial synthetic sorbent.

Once plant derived sorbents are applied to saturated environments, preferential water sorption is naturally favored over the sorption of oil because the sorbents are typically hydrophilic in nature. Agricultural by-products have well documented problems with water sorption and lack of dimensional stability due to their associated hydroxyl functionality. The hydroxyl groups that are abundantly available in all the major chemical components of plant-based materials are responsible for the hydrophilicity [6].

The use of sorbents to clean-up oil spills presents many advantages due to simplicity of the approach and the inexpensive nature of the materials. In addition, plant derived organic sorbents are biodegradable thus leaving no permanent residue. Agricultural by-products can be considered polymeric composites made up primarily of cellulose, hemicelluloses and lignin [12]. The hydroxyl functionality of these fibers can be reduced by chemical modification, such as acetylation, methylation, cyanoethylation, benzoylation, acrylation and acylation [11, 13].

Acetylation reaction is one of the most common techniques employed for hydrophobic treatment of linocellulosic materials (like wood) which involves a substitution reaction of a hydroxyl group (Hydrophilic) into an acetyl group (hydrophobic). Various catalysts have been used for enhancing the efficiency of acetylation reactions. Pyridine and 4-dimethyl amino pyridine (DMAP) have been commonly applied for acetylation for many years [13]. However, they are too toxic and (or) are expensive for commercial use. Sun et al. (2004) [11] reported that acetylation of sugarcane bagasse with N-bromosuccinimide (NBS) as catalyst in a solvent-free system was a convenient and effective method for enhancing the oil sorption capacity of the sorbent material.

2 Material and Methods

2.1 Materials

Cucurbita moschata seed husk (Igbo name: “Ogbene”/ “Obene mmanya”), were obtained from *Cucurbita moschata* seed in the Aba Abia state environment of Abia state, Nigeria. The mature seeds were collected after the fruits fell off the trees. Each seed was cracked open

manually and deseeded. The husks were washed with clean water, dried under the room temperature for 24 hours, then left to dry in the oven at 30^{o}C until constant weight was attained. The dried sponges were ground using a manual grinding machine and sieved. The portions that passed through size 25 British standard sieves and retained by size 36 were used for further analysis. Fig 1 shows digital images of the unmodified *Cucurbita moschata* seed. The crude oil samples were collected from Nigeria National Petroleum Corporation (NNPC) Port-Harcourt Nigeria.

Figure 1 Digital image of *Cucurbita moschata* seed

2.2 Methods

2.2.1 Acetylation of the unmodified *Cucurbita moschata* seed husks

The acetylation of the samples under mild conditions, in the presence of KBr and KI catalyst, using acetic anhydride was carried out using the method of Sun et al. (2004) [11]. The amount of substrate and reactant were combined in a ratio of 1:20. The reaction temperature was 30^{o}C, time was differently varied from 30 minutes to 240 minutes at 30 minutes intervals and the catalyst concentration varied from 0.2 g to 1.6 g at 0.2 g interval. The mixture of the raw sorbents, acetic anhydride and catalyst was placed in a round bottom flask fitted to a condenser. The flask was placed in an oil bath on top of a thermostatic heating device, thereafter, the flask was removed from the bath and the hot reagent was decanted off. The sorbents were thoroughly washed with ethanol and acetone to remove un-reacted acetic anhydride and acetic acid as by-products. The new products were dried in an oven at 60^{o}C for 16 hours prior to analysis. The degree acetylation was estimated from the infrared spectra by calculating the ratio (R) between the intensity of the acetyl C=O stretching band 1740 - 1745cm^{-1} and the intensity of the C-O stretching vibrations of cellulose backbone at about 1020-1040cm^{-1} as shown below [14].

$$R = \frac{I_{1740}}{I_{1020}} \tag{1}$$

2.2.2 Effect of acetylation duration

To determine the effect of acetylation duration on the samples, the acetylation reaction was allowed to take place for 30, 60, 90, 120, 150, 180 and 240 minutes using different samples and the degree of acetylation was estimated for the various durations. The data from this analysis were used for kinetic study of the acetylation processes.

2.2.3 Effects of catalyst concentration

To determine the effect of catalyst concentration on the samples 0.200 to 0.206g of the catalyst were used at room temperature. The degree of acetylation was estimated for the various catalyst concentrations after 1 hour of reaction.

2.2.4 Effect of contact time

To determine the effect of contact time on the crude oil adsorption behaviour of the adsorbents, samples were taken from the adsorption system after 1, 3, 5, 10 and 15 minutes of contact. The amount of crude oil adsorbed, as well as the sorption capacity of the adsorbents at each time interval were determined. The data from this analysis were used for kinetic and mechanism study of the adsorption processes.

2.3 Characterization of adsorbents

The topographical and morphological information about the sample were provided by SEM through the high-resolution, three dimensional and high depth-of-field images of the sample

surface and near-surface. The surface morphologies of the raw and acetylated adsorbents were observed with a scanning electron microscope using the method reported by Mohammed and Abdullah (2019) [15]; About 20 mg of the oven –dried samples were mounted on a metallic stub with a conductive carbon tape and coated with a thin layer of carbon to form a conductive layer around the sample and to prevent accumulation of electron beams. Micrographs of the samples were obtained after irradiation with a 20kv beam of electrons under vacuum. It revealed spatial variations in chemical compositions of the samples and their porous natures.

2.4 Crude oil sorption

In order to simulate the oil spill situation and to minimize experimental variation, the crude oil was held in a beaker for one day in open air to release volatile hydrocarbon contents. The sorption of oil from water was carried out using batch method as reported by Nwadiogbu et al. (2016) [16]. A portion 0.2 g of each of the raw and acetylated adsorbents was placed in a 250 mL beaker containing 10 g of the weathered crude oil displaced in 100 mL of water at 26^{o}C. The samples were left in the mixture for 15 minutes with little agitation. The sorbents were then removed from the beakers using sieving nets. Then the oil-loaded sorbents were dried at 60^{o}C for 30 minutes and re-weighed. The oil sorption capacity was calculated according to the standard method (ASTM F726-99) as shown in equation 3.14 [17].

$$Oil\ sorption\ capacity\ (g/g) \quad = \frac{W_1 \ - \ W_0}{W_0} \tag{2}$$

Where W_0 and W_1 are the weight of adsorbent before and after oil absorption, 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.

$$q_e \ = \ \frac{(C_0 \ - \ C_e \ ) \, V}{m} \tag{3}$$

Where C_0 is the initial crude oil concentration (mg/L), C_s is the equilibrium crude oil concentration (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent (g).

The effect of the adsorbent dose on the crude oil sorption behaviour of the adsorbents was also studied using weight size from 0.2, to 1.0 g of each adsorbent for a sorption duration of 5 minutes. The sorption processes were also performed using 50, 75, 100, 125, and 150 g/L of crude oil with 0.2g adsorbent for 5 minutes. Data obtained were used for equilibrium studies of the adsorption processes using the isotherm models stated in Table 1. The effect of contact time on the oil sorption behaviours of the adsorbents wasted by carrying out the sorption experiments for a duration of 5, 10, and 15 minutes. The kinetic models presented in Table 2 were used to investigate the sorption kinetics. Additionally, the sorption processes were performed at 30^{o}C, at operating conditions of 100 g/L crude oil, 0.2 g adsorbent, 5 minutes to determine the effect of time on the sorption capacity of the adsorbents and for thermodynamic studies of the adsorption processes.

2.4.1 Oil sorption capacity

The sorption of oil from water was carried out using the methods of Banerjee et al, (2006) [18]. To simulate the situation of oil spill and minimize experimental variation, the crude oil sample was held in beakers for one day in open air to release volatile hydrocarbon contents. The raw and acetylated samples were then subjected to crude oil sorption test. To 100 mL of distilled water in a 250 mL beaker, 5 g of crude oil was added. A portion (1 g) of the sorbent was added into the mixture in the beaker. The mixture was allowed to stand for about 3 minutes with little agitation. The sorbents were removed from the beakers using a sieve net and left to drain by hanging the net over the beaker in an oven for 30 minutes at 60^{o}C and weighed. The same procedure was repeated for the other four samples. The oil sorption capacity was calculated by taking into account the weight of sorbent, weight of sorbent and oil and weight of sieve net.

$$Oil\ sorption\ capacity\ (g/g) \quad = \frac{S_{st} \ - \ S_o}{S_o} \tag{4}$$

Where S_o is the initial mass of the dry sorbent, S_{st} is the mass of the sorbent with oil at the end of the sorption test and the ($S_{st} - S_o$) quantity is the net oil sorbed (all of the masses were measured in grams). The amount of crude oil adsorbed (q_e) in milligrams per gram was determined using the following mass balance equation;

$$q_e = \frac{(C_o \ - \ C_e) \, V}{m} \tag{5}$$

Where C_o is the initial oil concentration in mg/L, C_e is the equilibrium oil concentration in mg/L, V is the solution in liters, and *m* is the mass of the adsorbent in g.

Table 1 Selected isotherm models investigated

SN	Type	Linear form	Plot	Parameters	Reference
1	Freundlich model	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ *vs* $\ln C_e$	Slope = $\frac{1}{n}$; Intercept = $\ln K_F$	Diraki et al. (2018) [19]
2	Temkin model	$q_e = B \ln A + B \ln C_e$	q_e *vs* $\ln C_e$	Slope = B; Intercept = $B \ln A$	Rahangdale et al. (2018) [20]
3	Langmuir model	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	$\frac{C_e}{q_e}$ *vs* C_e	Slope = $\frac{1}{q_m}$; Intercept = $\frac{1}{K_L q_m}$	Mahmoud et al. (2020) [15]

Note: C_e is the equilibrium concentration of the adsorbate (mg/L), q_e and q_m are equilibrium and maximum monolayer adsorption capacities (mg/g), respectively. KL is the Langmuir constant (L/mg) and B are Temkin constants, and K_F [(mg/g)(L/g)$^{1/n}$} and n are Freundlich constants related to adsorption capacity and intensity, respectively.

Table 2 Selected kinetic models investigated

SN	Type	Linear form	Plot	Parameters	Reference(s)
1	First-order Kinetics	$\ln \Theta_t = \ln \Theta_0 - k_1 t$	$\ln \Theta_t$ vs t	k_1 = Slope; $\Theta_0 = e^{\text{Intercept}}$	Shin and Kim (2016) [21]
2	Hill second-order Kinetics	$\frac{1}{\Theta_t} = \frac{1}{\Theta_0} + k_2 t$	$\frac{1}{\Theta_t}$ vs t	Θ_0 = 1/Intercept; k_2 = Slope	Oloo et al. (2020) [22]
3	Pseudo-second-order Kinetics	$\frac{t}{\Theta_t} = \frac{1}{k_2 \Theta_0^2} + \frac{t}{\Theta_0}$	$\frac{t}{\Theta_t}$ vs t	Θ_0 = 1/Slope; k_2 = Slope^2/Intercept	Nwadiogbu et al. (2016) [16]
4	Intra-particle Diffusion	$\Theta = K_d t^{1/2} + C$	Θ vs $t^{1/2}$	K_d = Slope; C = Intercept	Nwadiogbu et al. (2016) [16]

2.5 Statistical analysis

Comparative adsorption between modified and unmodified samples was analyzed using two-way ANOVA test at a 95% confidence interval in excel version of 2010 p-values less than the 0.05 significance level showed significant variations in the mean values of oil sorption capacity.

3 Results and discussion

3.1 Scanning electron microscopy (SEM) analysis

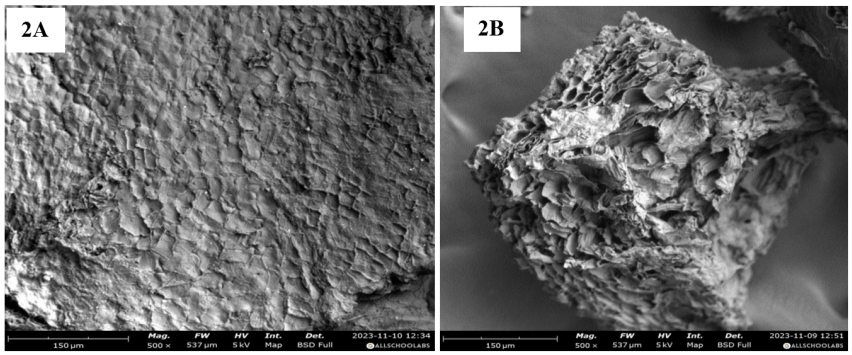

Figure 2 a. SEM micrograph image at mag.500 x for raw, (b): SEM micrograph image at mag.500 x for acetylated *Cucurbita moschata* seed husk

The morphology of the raw and acetylated *Cucurbita moschata* seed husk are presented in Fig. 2a, 2b respectively. Fig. 2a presents the surface and cross section of the raw *Cucurbita moschata* seed husk. The image reveals an irregular and rough surface with a wrinkled or crumpled appearance. The surface is not smooth, suggesting a complex microstructure. The wrinkled and irregular surface shows to have a high surface area, which is beneficial for adsorption and interaction with other materials. Some regions appear to have small depressions or pores, indicating possible porosity in the husk material. The presence of pores and cracks indicates potential permeability, which can influence moisture absorption and mechanical strength. The morphology shows a fibrous or layered structure, which may contribute to the mechanical properties of the seed husk. There are visible cracks or gaps, which could be due to natural growth patterns. This fibrous or layered structure suggests the presence of cellulose, hemicellulose, and lignin, which contribute to mechanical strength and flexibility. In Fig 2b shows the morphology of acetylated *Cucurbita moschata* seed husk, which has undergone

chemical modification The acetylated process changed the configuration of the sample, this became open pores and voids, indicating surface modification. The rough and porous structure suggests enhanced surfaced area, which can improve adsorption and reactivity. The image reveals more disputed and fragmented structure, possibly due to the breakdown of certain biopolymers (such as during acetylation [23]). The presence of layered formations suggests changes in lignocellulosic composition. The material appeared more irregular and jagged, which could be due to the structural rearrangements caused by acetylation. The cracks and broken layers indicate that the acetylation may have altered the mechanical properties, potentially reducing rigidity while enhancing flexibility. Some regions appear swollen or expanded, which might be due to acetyl groups modifying hydroxyl (-OH) groups in the cellulose, reducing hydrogen bonding and increasing hydrophobicity.

When compared with the raw sample the raw husk had more compact and fibrous structure, while the acetylated result shows a higher porosity, fragmentation, and structural breakdown. Acetylation improved the hydrophobicity and resistance to biodegradation, making the material more durable. These changes improve its suitability for adsorption [24].

3.2 FTIR analysis

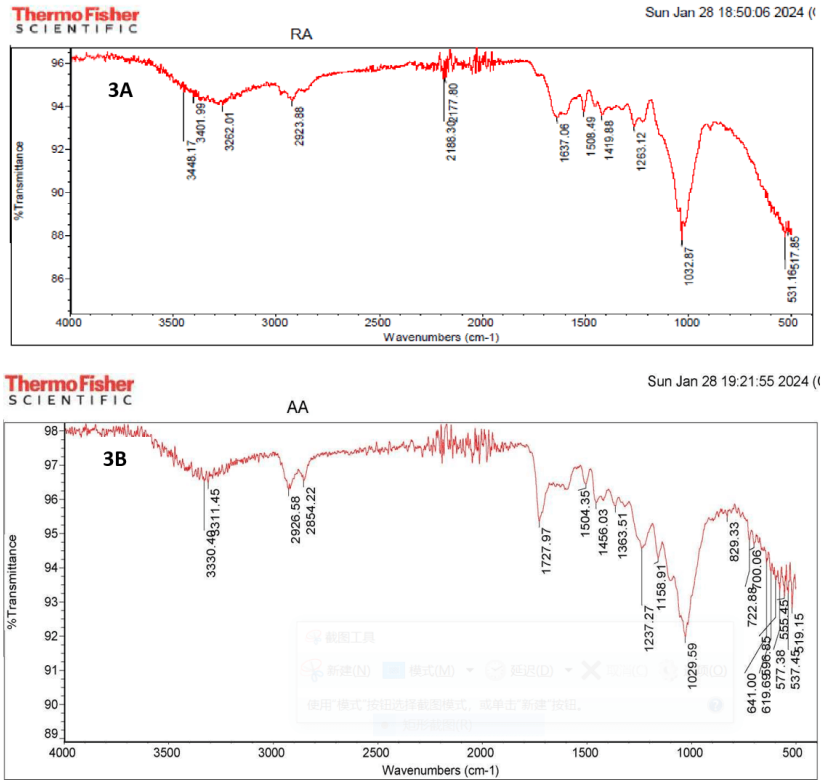

Figure 3 Spectra of (3A) raw (3B) acetylated *Cucurbita moschata* seed husk

The FTIR spectra of both untreated and acetylated *Cucurbita moschata* seed husk samples in the range 3448 to 519 cm-^{1} are shown in Figures 3a to 3b and all the major infrared absorption bands observed in the spectra. The peaks observed at 3448, 3401, 3262, 2923, 2188, 2177, 1637, 1508, 1419, 1263, 1032, 531 and 517cm^{-1} are associated with the raw *Cucurbita moschata* seed husk while those observed at 3330, 3311, 2926, 2854, 1727, 1504, 1456, 1363, 1237, 1158, 1029, 829, 722, 700, 641, 619, 596, 577, 555, 537 and 519 cm^{-1} in the spectra of the acetylated *Cucurbita moschata* seed husk provide some evidence of acetylation [25]. The hydroxyl stretching vibration region of the infrared spectra of untreated and acetylated *Cucurbita moschata* seed husk samples. The strong band at 3448 cm^{-1} 3311.45cm-^{1} are attributed to OH stretching vibrations suggesting the presence of alcohols or phenolic groups, and their broadness indicates hydrogen bonding due to acetylation [26]. As illustrated in Fig. 3a and Fig. 3b. The peak intensities at this OH stretching band at 3330 cm^{-1} in the acetylated samples was observed to be lower in the acetylated *Cucurbita moschata* seed husk spectra than in the raw sample spectra indicating some partial acetylation. However, it was observed that there

was a slight gradual increase in the intensity of the OH stretching band indicating a gradual lowering of the extent of acetylation as the reaction time is increased. This is in contrast to the results obtained by Sun et al. (2002) [27]. In their investigation of the acetylation of rice straw samples. Acetylation of cellulose is an equilibrium reaction just like any other esterification reaction such that de-acetylation can take place under appropriate reaction conditions [25]. It is therefore possible for de-acetylation to occur in the presence of the acetic acid by-product for the longer time reactions thereby leading to re-formation of the free hydroxyl groups of the *Cucurbita moschata* seed husk [28]. Evidence of acetylation is again clearly observed in Figures 3a and 3b by the presence of ester bonds at 1727cm^{-1} (carbonyl C=O stretching of ester or acetates), indicative of carbonyl-containing groups, likely from esterification in the acetylated sample. 1504 [C=C stretching) and 1456 cm^{-1}(CH_2 bending) suggests a conjugated aromatic skeletal vibration, possibly from benzene-like structures. and CH_2 bending in a scissoring motion respectively. 1237, 1158 and 1029cm^{-1} (C-O stretching of acetyl group) in the spectra of the acetylated samples. Fig. 3b also shows that there is no absorption in the region 1600 - 1500 cm^{-1} in the spectra of the acetylated *Cucurbita moschata* seed husk indicating that the acetylated products are free of the raw acetic anhydride [29, 30]. The absence of a peak at 1700 cm^{-1} for a carboxylic group in spectra indicates that the samples are also free of the acetic acid by-product. FTIR is sensitive enough to detect contamination with at least the by-product of the reaction [31]. There are changes due to acetylation increasing intensity at 577-519cm^{-1}The presence of C=O stretching at 1727cm^{-1} and C-O stretching bands confirms that acetylation of the sample changes the CH stretching and bending vibrations in the structural modifications [32]. The aromatic and out-of-plane bending vibrations suggest that some aromatic rings or conjugated systems remained unchanged after acetylation [33].

3.3 Adsorption tests

3.3.1 Effect of time on crude oil sorption onto *Cucurbita moschata* seed husk

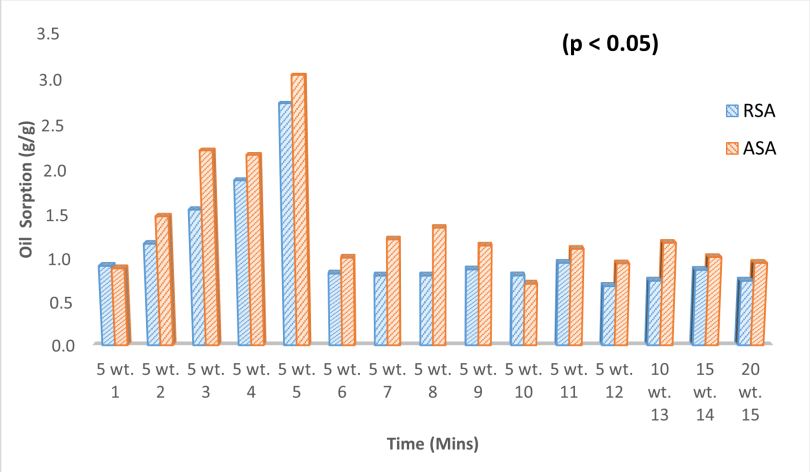

Figure 4 Effect of contact time on oil sorption capacity of raw and acetylated *Cucurbita moschata* seed husk

Fig 4. shows the effect of time on the oil sorption capacity for raw and acetylated *Cucurbita moschata* seed husk. The results of oil sorption capacity as expected increase with increase in sorption time from 5 to 20 minutes. In the early time of intervals, the raw and acetylated sample weight 1 to 15 showed a steady increase in oil sorption capacity. The ASA showed a higher oil sorption capacity than RSA suggesting that acetylation enhances the materials ability to absorb oil.

Maximum oil sorption capacity of 3.046g/g for ASA and 2737g/g for RSA was observed at 5 minutes respectively. The crude oil sorption capacity values for the acetylated sample was higher than those of the raw samples. This might be due to the absorption on the surface of the material and subsequent penetration into the inner microscopic voids of the acetylated samples [34]. The results further showed the fast and stable nature of the process as only a slight difference was observed between the initial and final contact time [16, 35]. After 5 minutes, the sorption capacity decreases significantly and then stabilize from 10 minutes onwards. This could indicate that the material reaches saturation, preventing further absorption of oil. It also shows that the material is time-dependent, with rapid absorption within the first few minutes.

The acetylated sample has higher oil sorption capacity than the raw sample, which shows the effectiveness of the acetylation in improving oil absorption. The decline in sorption capacity over time suggests that the sample becomes saturated after short period Figure 4 shows that ASA is more olephilic than RSA. This is due to the decrease in hydroxyl functionality of the RSA by acetylation [35]. The effect of variation of time (acetylated and Raw sample) was tested with ANOVA for statistical difference.

3.4 Equilibrium studies

3.4.1 Adsorption Isotherm model studies for *Cucurbita moschata* seed husk

Adsorption equilibrium studied was done using adsorption isotherms to determine the surface properties of the adsorbents. The Freundlich, Langmuir and Temkin isotherms, as expressed in Table1 and presented in fig 5a-5f.

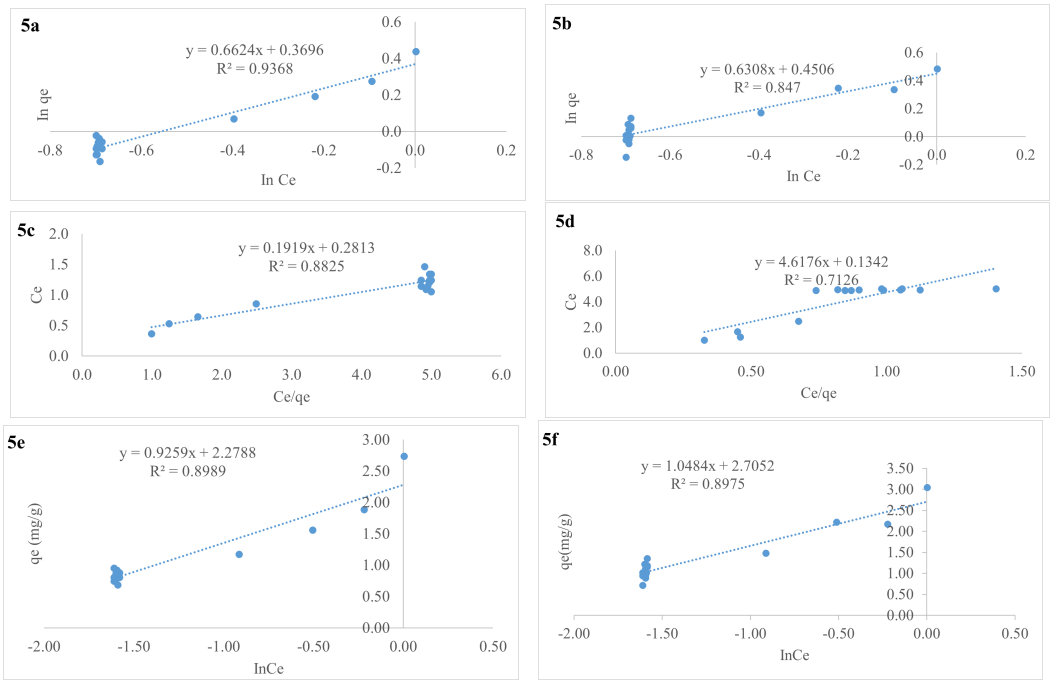

Figure 5 5a: Freundlich model (raw); 5b: Freundlich model (acetylated); 5c Langmuir model (raw); 5d: Langmuir model (acetylated); 5e: Temkin model (raw); 5f: Temkin model (acetylated) of crude oil adsorption for *Cucurbita moschata* seed husk.

Table 3 Isotherm parameters for crude oil adsorption on unmodified and modified *Cucurbita moschata* seed husk

Isotherm model	RSE	ASE
Freundlich model		
Intercept (log K_F)	0.3696	0.4506
n (g/L)	1.510	1.586
K_F (g/g)(L/g)$^{1/n}$	1.447	1.569
R^2	0.9368	0.847
Langmuir model		
Q_0 (1/slope) (g/g)	5.210	0.2165
$1/Q_0$ (slope)	0.1919	4.6176
Intercept ($1/Q_0B$)	0.2813	0.1342
B (L/mg/g)($1/Q_0\times$ intercept)	0.682	34.42
R^2	0.8825	0.7126
Temkin model		
Intercept	2.2788	2.7052
Slope	0.9259	1.0484
R^2	0.8989	0.8975
b (J/mol) (Temkin Constant at 30°C)	2735.2	2401.8
K_T (L/g) (Temkin Binding constant at 30°C)	9.72	13.22

The sorption isotherms of crude oil on the samples were studied at a constant temperature of

30^oC. The increase and decrease in the RSA and ASA (Table 3) indicated that the oil removal was dependent on the initial oil concentration. The reproducibility increased as the optimum pick-up was approached until they became constant. As oil increased in concentration, the sorption capacity of *Cucurbita moschata* seed husk also increased until it reached a highest point. The data above shows the sorption isotherms of the raw and acetylated *Cucurbita moschata* seed husk. The effect of acetylation is also observed in the chart

The results above showed that the acetylation of *Cucurbita moschata* seed husk in the presence of a catalyst enhanced the equilibrium of the sorbents towards crude oil. To facilitate the estimation of the sorption capacities, the experimental data were fitted into the Langmuir and the Freundlich isotherm models. The Langmuir and Freundlich isotherms are the most commonly used solid to liquid phase isotherms. These isotherms relate the amount of oil sorbed at equilibrium per unit weight of sorbent, Q_e (mg/g) to the sorbate concentration at equilibrium, C_e (mg/L). According to the Langmuir's model, adsorption occurs uniformly on the active sites of the sorbent, and once an adsorbate occupies a site, no further sorption can take place at that site [21, 36].

In the Langmuir's model, the mass of the solute sorbed per unit mass of sorbent (qe), increases linearly by increasing the solute concentration at low surface coverages [16, 37]. The isotherm constants and their correlation coefficients, R^2, are listed in Fig. 5a - 5f shows the Freundlich, Langmuir and Temkin model for the raw and acetylated *Cucurbita moschata* seed husk. $\log Q_e$ against $\log C_e$ is plotted and the constants may be evaluated from the slope n and the intercept Plot of $\log Q_e$ against $\log C_e$ is given in figure 5. The summary of isotherm constants and their correlation coefficients, R^2 (are listed in Table 3). The magnitude of the exponent, n gives an indication of the favorability of the adsorption. It is generally stated that values of n in the range 2-10, 1-2, less than 1 represent good, moderately difficult and poor sorption characteristics respectively, indicating that the sorption process is good. Similar results were produced when a range of modified cellulose materials as sorbents were used for crude oil sorption by Okoro and Ejike (2007) [38]. The graph of Temkin isotherm in Fig 5e and Fig 5f representing the adsorption for raw and acetylated *Cucurbita moschata* seed husk, its R^2value of 0.8989 and 0.8975 respectively, indicating a strong correlation, suggesting that the adsorption follows the Temkin model. The positive slopes indicate a good interaction between the adsorbate adsorbent. It also suggests that adsorption increases more significantly with increased InCe, (that at a higher concentration, adsorption is more effective). The higher b value means that the first system requires more energy for adsorption, suggesting stronger adsorbate-adsorbate interactions that affect adsorption. The model assumes adsorbate-adsorbate interactions, this result suggests that the adsorbate molecules are likely influencing each other during adsorption. Fig. 5f has a higher K_T value than the values in Fig 5e which suggests that the adsorbate has a stronger affinity for the adsorbent, leading to a higher adsorption capacity. It also suggests that Fig 4.96 has a more efficient adsorption process compared to the values in Fig. 5e.

Based on the coefficient of determination values R^2, it can be concluded that the experimental data better fitted the Temkin model than the Langmuir and Freundlich model as the R^2 values of the Temkin model tend to be much closer to 1 than those obtained from the Freundlich and Langmuir isotherm. The values of the coefficient of determination indicated that the acetylated *Cucurbita moschata* seed husk. is an excellent biomaterial for the removal of oil from aqueous environments [39].

3.5 Kinetic studies

3.5.1 Kinetic studies of crude oil sorption on *Cucurbita moschata* seed husk

Fig. 6a represents the first order kinetic model for the sorption of the raw *Cucurbita moschata* seed husk. The low R^2 value (0.0306) suggests that it is a poor fit to the first order kinetics. The coefficient of determination R^2 is very low, indicating that the data does not fit well with the first order kinetic model. This suggests that oil sorption onto the raw *Cucurbita moschata* seed husk does not follow first order kinetics and may follow a different kinetic model. The rate of the constant K= 0.0142 is relatively low, implying that the sorption process is slow. This could be due to diffusion limitations, weak interactions between oil and the raw *Cucurbita moschata* seed husk. The calculated equilibrium sorption capacity from the intercept is qe = 1.34mg/g, which is quite low. This indicates that the *Cucurbita moschata* seed husk may have limited oil adsorption capacity under the given conditions.

Fig. 6b represents the first order kinetic model for the sorption of the acetylated *Cucurbita moschata* seed husk; the R^2 value (0.0761) is also poor to fit the first order kinetics. Indicating that the first order kinetic model does not adequately describe the sorption process. The weak

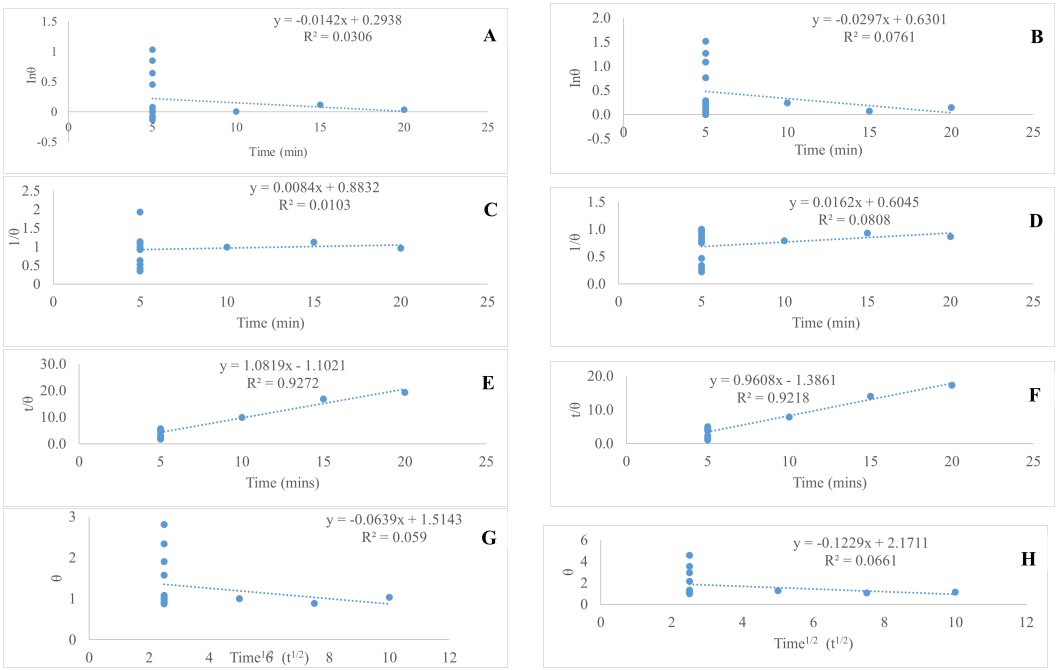

Figure 6 (a) First order (raw); (b) First order (acetylated); (c) Second order (raw); (d) Second order (acetylated); (e) Pseudo-second order (raw); (f) Pseudo-second order (acetylated; (g) Intra-particle diffusion; (h) Intra-particle diffusion (acetylated) kinetic model(s) for crude oil sorption of *Cucurbita moschata* seed husk.

correlation suggests that another mode may provide a better fit. The rate of constant $K_1 = 0.0297$ is slightly higher than that of the raw *Cucurbita moschata* seed husk, implying that acetylation enhances the sorption rate. This increase suggests that chemical modification improved the *Cucurbita moschata* seed husk affinity for oil. The expected sorption capacity, when calculated is 1.88 which is higher than the Qe of the raw *Cucurbita moschata* seed husk= 1.34. This increase in Qe further supports the idea that acetylation improved the oil sorption capacity. The low R^2 suggests that oil sorption on acetylated *Cucurbita moschata* seed husk does not follow first order kinetics.

Fig. 6c represents the second order kinetic model for the sorption of the raw *Cucurbita moschata* seed husk. A low value of K_2 was observed, suggesting a slow sorption process, indicating a weak interaction between the oil and the adsorbent. The calculated Qe is relatively low, suggesting that the adsorbent has a moderate to low capacity for oil sorption. The R^2 (0.0103) shows that the model does not fit the data well, suggesting that the sorption process does not follow the Hill second order of kinetic model for sorption of oil on raw *Cucurbita moschata* seed husk effectively. The low R^2 suggests that other kinetic models may describe the sorption process better. The low K_2 value implies that the adsorption rate is slow, possibly due to surface resistance, poor affinity between oil and the adsorbent. The relatively low Qe value suggests that the material may not be highly efficient for oil sorption, that equilibrium is reached quickly with minimal sorption.

Fig. 6d represents the Hill second order kinetic model for the sorption of the acetylated *Cucurbita moschata* seed husk. The K_2 (0.0162) which represents the second order rate constant (K_2) when compared to the raw *Cucurbita moschata* seed husk, has a higher value. Suggesting that acetylation may have improved the adsorption kinetic, leading to a slightly faster sorption process. The R^2 value of 0.0808 indicates a very weak correlation between the model and the experimental data. The low R^2 implies that other kinetic models might better describe the sorption process. The acetylation introduces hydrophobic functional groups, which could increase the affinity of the adsorbent for oil. Although this second order model suggests an improved sorption rate (higher K_2), the poor R^2 value indicates that the adsorption process is likely controlled by other mechanisms.

Fig. 6e represents the Pseudo-second order kinetic model for the sorption of the acetylated *Cucurbita moschata* seed husk. The coefficient of determination R^2 0.9272 suggests a strong correlation between the experimental data and the kinetic model. This high R^2 value confirms that the adsorption of the oil on raw *Cucurbita moschata* seed husk follows the pseudo-second

Table 4 Kinetic parameters for crude oil sorption on *Cucurbita moschata* seed husk

Type	Raw sample *Cucurbita moschata* seed husk	Acetylated Sample *Cucurbita moschata* seed husk
First-order kinetics		
Intercept	0.2938	0.6301
q_e^{calc} (mg/g)	1.34	1.88
R^2	0.0306	0.0761
K_1 (min^{-1})	0.0142	0.0297
Second-order kinetics		
Intercept	0.8832	0.6045
q_e^{calc} (mg/L)	1.1322	1.6543
R^2	0.0103	0.0808
K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	0.0084	0.0162
Pseudo-second-order kinetics		
Intercept	1.1021	1.3861
q_e^{calc} (mg/L)	0.9243	1.041
R^2	0.9272	0.9218
K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	1.0819	0.9608
Intra-particle diffusion		
K_d ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$)	-0.0639	-0.1229
C (mg/g)	1.5143	2.1711
R^2	0.0590	0.0661

order model well. The calculated equilibrium adsorption capacity Qe suggests that the raw *Cucurbita moschata* seed husk has a moderate ability to adsorb oil. The pseudo-second order rate constant K_2 indicates how quickly the system reaches equilibrium.

In Fig. 6f, it shows the Pseudo Second order kinetic model for sorption of oil on acetylated *Cucurbita moschata* seed husk. The co-efficient of determination R^2 0.9218 suggests that the pseudo-second order model provides a good fit for the data. Comparing the value here with the raw sample, the both samples showed strong values confirming that the pseudo-second order model is appropriate.

Fig. 6g represents the intra-particle model for oil sorption using raw *Cucurbita moschata* seed husk as the adsorbent. The low R^2 indicates a very weak fit of the intra-particle diffusion model to the process. The negative slope is unusual; as intra-particle diffusion models yield a positive slope when diffusion controls adsorption. A higher intercept (C) suggests a significant boundary layer effect.

Fig. 6h Intra-Particle order kinetic model for sorption of oil on acetylated *Cucurbita moschata* seed husk. The R^2 0.0661is very low when compared to the other models analyzed. Indicating a very poor fit of the intra-particle diffusion model. The negative slope (K_d- -0.1229) indicates limitations in the model's applicability. The larger intercept suggests a significant boundary layer effect. From Fig. 6g and Fig. 6h, it is observed that intra-particle diffusion is not the dominant mechanism for oil sorption on the raw and acetylated Cucurbita *moschata* seed husk.

4 Conclusion

The raw seed husk has an irregular and rough surface with a wrinkled or crumpled appearance, indicating a complex micro-structure and high surface area, which is beneficial for adsorption and interaction with other materials.

The acetylated seed husk has undergone chemical modification, which changed its configuration, opened pores and voids and altered its mechanical properties, potentially reducing rigidity while enhancing flexibility. The acetylation process improved the hydrophobicity and resistance to moisture sorption of the material, making it more durable. The acetylation changed the morphology of the seed husk, making it more suitable for certain applications the acetylated seed husk has undergone chemical modification, which changed its configuration, opened pores and voids, and altered its mechanical properties, potentially reducing rigidity while enhancing flexibility.

The acetylation process improved the hydrophobicity and resistance to moisture sorption of the material, making it more durable. Both raw sample (RSC) and acetylated sample show rapid initial increase in oil sorption capacity, reaching a maximum at around 5 minutes. After this peak, their capacities decrease slightly and level off as the sorption sites become saturated and equilibrium is reached. ASC has a higher maximum oil sorption capacity and a faster initial

sorption rate than RSC. The acetylated sample indicates monolayer adsorption on uniform sites. It has higher capacity than the RSC. Temkin model shows strong adsorbate-adsorbent interaction. ASC has a higher Temkin constant (b) and binding constant (K_t), indicating stronger and more efficient adsorption. ASC demonstrates better adsorption properties than RSC, with higher capacity, stronger binding, and faster adsorption. Isotherm analysis confirms that modified seed husk is an effective sorbent for r crude oil removal.

Authors contribution

Ajiwe Adaku Chinonyerem: Writing – original draft, review and editing, Methodology, Data curation, Conceptualization, Software, Formal analysis.

Patrice-Anthony Chudi Okoye: Review & editing. Uche Eunice Ekpunobi: Writing – review & editing, Resources.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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