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Enhanced Hydrophobicity and Oleophilicity for the Removal of Crude Oil from Aqueous Medium Using Modified Coconut Coir Activated Carbon (CCAC) and Empty Palm Fruit Bunch Activated Carbon (EPFBAC)

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Abstract

Crude oil spillage has tremendous environmental impacts and poses severe pollution problems worldwide due to the continuous activities and operations in the oil and gas sector. This has resulted in the urgent need for clean-up techniques such as the use of natural adsorbents which are considered a low-cost, readily available, efficient, eco-friendly, and easy-to-deploy method of handling oil spillage due to their high oil sorption capacity, high oil selectivity, oleophilic, enduring, reusability and biodegradable properties. Empty palm fruit bunch (EPFB) and coconut coir were used as precursors to produce activated carbon (modified with Lauric acid solution) for oil spill remediation. The influence of varying parameters was investigated using a batch experimental procedure and the results showed that the crude oil adsorption capacity increased with a corresponding increase in contact time, initial oil concentration, temperature, agitation speed, and particle size but a decrease in adsorbent dosage. The combination of surface morphological modification and hydrophobicity enhancement resulted in significantly improved adsorption capacity for crude oil removal (2710.0 mg/g and 4859.5 mg/g for $EPFBAC_{L.A}$ and $CCAC_{L.A}$ respectively), as evidenced by both FTIR and SEM analyses. The experimental isotherm data were analysed using various isotherm models and the best-fitted isotherm model was the Freundlich model with a correlation coefficient ($R^2 = 0.991$ and $R^2 = 0.999$) for $EPFB_{L.A}$ and

$CCAC_{L.A}$ respectively. The kinetic behaviour of the adsorption process was best described by pseudo-second order with R^2 values of 0.970 and 0.999 for $EPFBAC_{L.A}$ and $CCAC_{L.A}$ respectively while Boyd model revealed that the adsorption was controlled by an internal transport mechanism and film diffusion was the rate-limiting step. The crude oil adsorption was chemisorption and endothermic owing to the positive enthalpy values (ΔH^o = 183.890 KJ/mol for $EPFBAC_{L.A}$ and ΔH^o = 69.656 KJ/mol for $CCAC_{L.A}$), the positive value of entropy (ΔS^o = 0.68 KJ/mol·K for $EPFBAC_{L.A}$ and ΔS^o = 0.295 KJ/mol·K for $CCAC_{L.A}$) suggested that the adsorption process was accompanied by an increase in the degree of randomness or disorder at the interface between the adsorbent and the adsorbate. A temperature rise led to a decline in Gibbs energy (ΔG^o), suggesting that adsorption became more feasible and spontaneous at higher temperatures and the significant activation energies for $EPFBAC_{L.A}$ (E_a = 183.889 KJ/mol) and $CCAC_{L.A}$ (E_a = 69.656 KJ/mol) indicated the existence of a substantial energy barrier that must be overcome to initiate the reaction. The results from the prepared adsorbents showed the significant capability to be used as a low-cost, re-generable and eco-friendly adsorbent in oil spill clean-up and is recommended to exploit its usage on a large scale.

Subject Areas

Chemical Engineering, Environmental Chemistry, Physical Chemistry

Keywords

Wastewater Treatment, Biomass Waste Management, Adsorption Capacity, Crude Oil Spillage, Activated Carbon

1. Introduction

The progressive increase of industrialization in Nigeria and the world has resulted in a continuous increase in environmental pollution due to the over-reliance on the use of fossil fuel and petroleum products for energy generation. Despite recent technological advances, accidental crude oil spillage and its refined products occur frequently during routine operations of exploration, extraction, transportation, storage, refining and distribution which has resulted in environmental degradation and economic losses [1]. Consequently, serious efforts have been devoted to reducing these hazardous pollutants such as PAHs, CO_2, NO_x and thereby avoiding their dangerous and harmful effects on animals, plants and humans [2]. The constant negligence of the oil exploration companies has resulted in water bodies being polluted leading to the destruction of useful aquatic lives; farmlands rendered un-cultivatable due to loss of soil fertility, bioaccumulation of heavy metals on grown crops due to crude oil polluted soils and the spontaneous increase in related diseases; economic losses due to sporadic shut down in production operations as a result of pipeline vandalism [2]-[4]. Oil spills in water pose significant environmental hazards, necessitating effective removal methods such as mechanical (skimmers, boomers), biological (bioremediation, phytoremediation), chemical (dispersants, solidifiers, emulsion breakers) and adsorption (natural sorbents, zeolites, synthetic polymers, activated carbons) employed to address this challenge [5]. Amongst these several chemical and physical methods, the adsorption technique using activated carbon is considered to be superior to other techniques because of its capability to efficiently adsorb a wide range of different types of adsorbates; its simplicity of design and is considered a more economically viable process for the treatment of oil spillage [6]. The choice of method depends on various factors such as the type of oil spilt, the extent of the spill, the environmental conditions, and the sensitivity of the affected area. However, commercial activated carbons are considered expensive which has led to many researches into cheaper and more viable substituents that are less expensive, biodegradable, reusable, environmental-friendly and are endowed with reasonable adsorptive capacities [7]. Hence, the efficiency of the adsorption process lies in choosing the suitable adsorbent which should be easily and readily available with no economic value [8]. Recently, several waste materials particularly from agricultural waste products whose disposal has been an environmental problem have been successfully utilized as precursors to produce activated carbons for the adsorption of oil in water. This has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly agricultural and industrial by-products, such as the male flower of coconut tree [9], avocado seed [10] [11], coconut shell [12], jute fibre [13], rubber wood sawdust [14], corncob [15], coconut coir/husk [16], oil palm fruit empty bunch [17] [18], bamboo [19] and oil palm fibre [20].

Oil palm (*Elaeis guineensis*) is mostly cultivated as a source of palm oil production in tropical regions such as Nigeria in West Africa and several other countries such as Malaysia, Indonesia, and Thailand in Southeast Asia etc and has resulted in the exponential generation of waste such as empty palm fruit bunch (EPFB), palm mesocarp fiber (PMF), palm kernel shell (PKS), palm oil mill effluent (POME) and boiler ash etc, which further creates enormous environmental challenges such as fouling, the attraction of pests, emission of greenhouse gases (GHGs), underground water pollution, thermal shock and emission, soil acidification etc, thus; posing serious threats to humans and the environment [21]-[23]. It was projected that by the year 2020, 49 MT/yr of palm oil produced would generate an estimated 19.6 MT/yr of waste [24]. Empty palm fruit bunch (EPFB) is considered a lignocellulosic material as it consists of an average estimate of (30% - 50%) cellulosic content, (15% - 35%) hemi-cellulosic content with hydrophilic properties and (20% - 30%) lignin content with hydrophobic properties and has strong structural stability properties, thus; it has a great potential as a basic precursor for the production of activated carbon (adsorbents) when chemically modified to adsorb pollutants such as dye, heavy metals, crude oil and petroleum products [25]-[27]. Lauric acid (used as a chemical activating agent) is a substance with a high hydrophobicity degree that tends to aggregate or dissolve in non-polar solvents or phases rather than in water. This behaviour arises because hydrophobic substances are typically non-polar or have non-polar regions that minimize their interaction with polar water molecules. The measurement or assessment of hydrophobicity degree can be important in determining how a substance behaves in different environments, including its solubility, dispersal characteristics, and interactions with other substances. It plays a significant role in fields such as drug delivery, environmental remediation, and surface chemistry. Hence, this research aimed to utilize modified adsorbents by enhancing the hydrophobicity and surface morphology of the adsorbents for the recovery of oil spilt in an aqueous solution.

2. Experimental Methods

2.1. Materials

The Empty Palm Fruit Bunch (EPFB) and coconut coir used in the preparation of the activated carbon were obtained from the National Institute for Oil Palm Research (NIFOR) in Abak Local Government Area, Akwa Ibom State, Nigeria. The crude oil used was obtained from Sterling Oil Exploration & Energy Production Company Ltd (SEEPCO), Nigeria.

2.2. Preparation of Adsorbent

The Empty Palm Fruit Bunch (EPFB) and coconut coir were washed using distilled water thereafter dried to constant weight at 105˚C for 24 h in a laboratory drying oven (DHG-9101 model) to remove excess water content and other volatile component. The crushed samples were carbonized in a muffle furnace at the temperature of 700˚C for 1 h in the absence of oxygen. The samples were impregnated by immersing them in a 30% concentration of diluted Phosphoric acid (H_3PO_4) solution for 24 h and thereafter dried in a laboratory drying oven at a temperature of 105˚C for 12 h. To enhance the hydrophobicity of the adsorbents (EPFBAC and CCAC), the pre-treated samples were further activated by pouring 2.0 L of boiled 0.4 M Lauric acid solution into a container containing 75 g each of EPFBAC and CCAC. The mixtures were stirred and kept for 12 h before being filtered and the resultant adsorbent samples were washed with n-hexane several times to remove any excess Lauric acid solution before being dried in a laboratory drying oven at 80˚C. The % Weight Gain (W.G) of the EPFBAC and CCAC were calculated according to Equation (1).

$$(\%)\text{W.G} = \left(\frac{\text{pre-treated weight} - \text{original weight}}{\text{original weight}}\right) \times 100 \tag{1}$$

The hydrophobicity degree (H.D) of $\text{EPFBAC}_{\text{L.A}}$ and $\text{CCAC}_{\text{L.A}}$ refers to the extent to which the materials or substances tend to avoid or repel water, preferring to interact with non-polar substances. In this experiment, 1.0 g of the adsorbents were placed separately in a beaker with 20 mL of water and agitated for 5 min. This was followed by adding 20 mL of n-hexane to the beaker and agitating it for 5 min. The mixtures were kept for 15 min for the two immiscible phases to separate. The adsorbents were subsequently filtered, dried and weighed to determine the actual amount that was being transferred to the organic phase and the result expressed in terms of the percentage of adsorbent transferred into the organic phase. The degree of hydrophobicity of the adsorbent was calculated based on Equation (2).

$$(\%)\text{H.D} = \left(\frac{\text{weight of adsorbent in n} - \text{hexane}}{\text{original weight}}\right) \times 100 \quad (2)$$

The activated carbons (EPFBAC$_{L.A}$ and CCAC$_{L.A}$) produced were allowed to cool and later crushed and sieved into various particle sizes (63 µm to 500 µm) and thereafter labelled and stored in air-tight enclosed plastic containers.

2.3. Proximate Analysis

The physicochemical properties of EPFBAC$_{L.A}$ and CCAC$_{L.A}$ was determined using proximate analysis to determine the moisture content [28], the volatile matter content [29], the ash content [30], the bulk density [31], pH [32] and the specific surface area [33].

2.4. SEM and FTIR Analysis of the Adsorbents

Scanning electron microscope (SEM) photographs of EPFBAC$_{L.A}$ and CCAC$_{L.A}$ were obtained by using the SEM machine (JEOL JSM-6360LV) when about 20 mg of the samples were sputter-coated with a platinum layer in a sputtering machine (Eiko IB-5 Sputter Coater) which was operated in an Argon atmosphere using a current of 6 mA for 3 mins and the SEM machine was left for 2 mins to stabilize before setting the parameters to be used. The coated samples were then transferred to the SEM specimen chamber and the imaging was done at an accelerating voltage of 15 kV, pressure at 0.003 Pa, eight spot size, four aperture and set at 1000 magnification.

Fourier transform infrared spectroscopy (FTIR) of EPFBAC$_{L.A}$ and CCAC$_{L.A}$ was done by using an FTIR Spectrometer (Perkin-Elmer SPECTRUM-2000) where the samples were dried and 2 mg of each sample was powdered and mixed with 300 mg of anhydrous KBr (Merck). The mixed samples were then pressed under vacuum to obtain the pellets for spectroscopy and the FTIR spectra were investigated between the wavelength ranges of 400 - 4000.0 cm^{-1}.

2.5. Batch Adsorption Equilibrium and Kinetics Studies

The experimental procedure for the batch adsorption studies was carried out by measuring 250 mL of the synthesized crude oil spill into a 500 mL beaker and was performed for different parameters such as contact time, mass of adsorbent, initial crude oil concentration, agitation speed, particle size and temperature. The batch adsorption equilibrium studies were carried out separately for EPFBAC$_{L.A}$ and CCAC$_{L.A}$ by measuring exactly 2.5 g of the adsorbents into a 500 mL beaker containing varying initial concentrations (11,664, 19,440, 27,216, 34,992 and 42,768 mg/L) of the synthesized oil spill and then agitated using an orbital shaker (Rotamax 120, Reidolph) at 20 rpm for 1 h. The adsorbed $\text{EPFBAC}_{\text{L.A}}$ and $\text{CCAC}_{\text{L.A}}$ were filtered off and the filtrate was thereafter homogenized for 30 mins to form an emulsified solution. The equilibrium concentration of the emulsified solution for each measured sample was determined using a UV-Vis spectrophotometer at a wavelength of 380 nm. Similarly, the batch adsorption kinetic studies were also carried out separately for $\text{EPFBAC}_{\text{L.A}}$ and $\text{CCAC}_{\text{L.A}}$ by measuring exactly 2.5 g of the adsorbents into a 500 mL beaker containing 19,440 mg/L initial concentration of the simulated oil spill and agitating it in an orbital shaker at 20 rpm and a temperature of 25˚C for varying contact time of (5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 min).

For each batch run, the amount of crude oil adsorbed per unit mass of activated carbon at equilibrium q_e, (mg/g), at time, t, q_t (mg/g) and the % removal of crude oil was determined using Equation (3), Equation (4) and Equation (5) respectively.

$$q_e = \frac{(C_o - C_e)*V}{M} \tag{3}$$

$$q_t = \frac{(C_o - C_t)*V}{M} \tag{4}$$

$$\%\ removal\ of\ crude\ oil = \frac{(C_o - C_e)*100}{C_o} \tag{5}$$

where C_o = initial concentration of solution (mg/L), C_e = equilibrium concentration (mg/L), C_t = concentration of solution at time, t, (mg/L), V = volume of the solution (mL) and M = mass of adsorbent used (g).

2.6. Thermodynamics Studies

As similarly described in the batch adsorption equilibrium and kinetics studies, the thermodynamics studies were also conducted separately when using $\text{EPFBAC}_{\text{L.A}}$ and $\text{CCAC}_{\text{L.A}}$ by using a Laboratory thermostatic shaking water bath (Model DKZ. XMTD-8222) at 20 rpm and at varying temperatures of (23˚C, 25˚C, 27˚C, 29˚C and 31˚C) for 1 h. The thermodynamics parameters such as Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o), entropy change (ΔS^o) and activation energy were used to describe the thermodynamic behaviour of the adsorption of crude oil onto $\text{EPFBAC}_{\text{L.A}}$ and $\text{CCAC}_{\text{L.A}}$ as shown in Equation (6), Equation 7 and Equation (8) respectively.

The Gibbs free energy change (ΔG^o) was calculated by using Equation (6).

$$\Delta G^o = -RTInK_c \tag{6}$$

where; K_c is the equilibrium constant of the adsorption which is obtained from Equation (6.1).

$$K_c = \frac{C_e(adsorbent)}{C_e(solution)} \tag{6.1}$$

where C_e (adsorbent) and C_e (solution) are the equilibrium concentration of the crude oil on the adsorbent and in the solution respectively.

The enthalpy change (ΔH^o) and entropy change (ΔS^o) were estimated from the slope and intercept of the plot of In K_c versus (1/T) respectively as shown in Equation (7).

$$InK_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{7}$$

Also, the activation energy was calculated from the slope of the plot of In K_c versus (1/T) as shown in Equation (8).

$$InK_c = InA - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{8}$$

3. Results and Discussion

3.1. Characterization of Adsorbent

As shown in **Table 1**, $EPFBAC_{L.A}$ and $CCAC_{L.A}$ had a low ash content of <5.0% which indicates some functional properties to be used to produce porous carbon with high yield. It is shown that various organic materials can be transformed into highly carbonaceous activated carbon depending on the type and concentration of chemical activator used as a typical ash content of activated carbon is <10%. The presence of excess ash in activated carbon tends to impede the pores and invariably reduce the surface area of activated carbon; thus, decreasing the adsorptive properties of activated carbons [34] [35].

The moisture content of $EPFBAC_{L.A}$ and $CCAC_{L.A}$ was shown to be <5.0% which met the standard requirements for packaging, transporting and storage of materials required for some commercial activated carbons [33].

Table 1. Proximate analysis of adsorbents.

Physical Properties	$EPFBAC_{L.A}$	$CCAC_{L.A}$
Specific surface area (m^2/g)	701.400	791.000
Moisture content (%)	1.800	1.500
Bulk density (g/cm^3)	0.333	0.370
Volatile matter content (%)	1.110	1.500
Ash content (%)	0.620	1.530
Ph	7.120	6.820
Weight Gain (%)	2.300	2.300
Hydrophobicity Degree (%)	70.000	80.000

The volatile matter content of 1.11% and 1.5% for $EPFBAC_{L.A}$ and $CCAC_{L.A}$ respectively is an indication of the additional influence of the chemical activators such as Phosphoric acid and Lauric acid in changing the surface structure by degrading the organic material of the biomass and enhancing the adsorptive properties of the activated carbon [36]. The pH level was slightly alkaline which is suitable for neutralizing an acidic soil and favouring the adsorption of cationic pollutants due to the electrostatic interactions between the adsorbate and the adsorbents [37].

3.2. FT-IR Analysis of the Adsorbents

The FT-IR spectra of EPFBAC$_{L.A}$ before and after adsorption were observed to have similar functional groups as that of CCAC$_{L.A}$ before and after adsorption is shown in Table 2. An absorption band revealed the presence of various functional groups which played a crucial role in the adsorption of crude oil molecules onto the surface and pore space of the adsorbents as enumerated in Table 2 [38]-[42]. The presence of hydroxyl (-OH) group on the surface of the adsorbent hypothetically repelled the crude oil molecules in the adsorption medium; thus, reducing the adsorption uptake [43] [44].

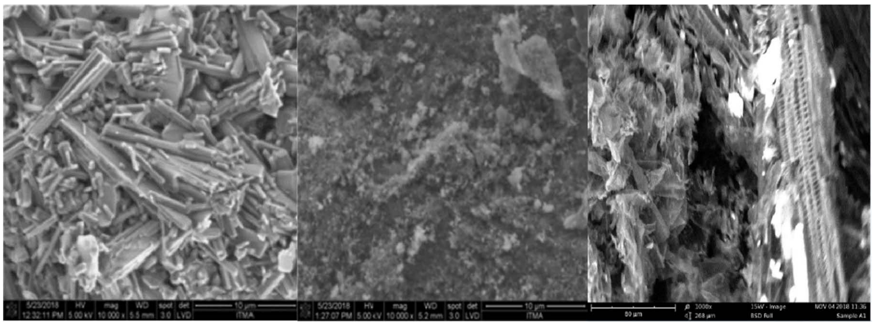
However, the introduction of chemical activating agents (Lauric acid) to the raw empty palm fruit bunch and coconut coir fibre which are rich in the hydroxyl group of cellulose, hemicellulose and lignin, encouraged esterify the cation process to occur [45]. Thus, the replacement of hydroxyl groups with the alkyl chain from the chemical activating agents led to the creation of a non-polar layer on the surface of the adsorbents. It is also believed that the increase in the hydrophobicity degree and the contact area of both EPFB$_{L.A}$ and CCAC$_{L.A}$ adsorbent enhanced and provided more superior sites for higher oil adsorption capacity. Hence, these enhanced hydrophobic functional groups for both EPFB$_{L.A}$ and CCAC$_{L.A}$ confirmed that crude oil was adsorbed at the hydrophobic sites of the adsorbents [46] [47].

Table 2. FT-IR analysis of the functional groups in the adsorbents.

Functional groups present in the Adsorbents	Absorption peaks of EPFBAC$_{L.A}$ before Adsorption (cm^{-1})	Absorption peaks of EPFBAC$_{L.A}$ after Adsorption (cm^{-1})	Absorption peaks of CCAC$_{L.A}$ before Adsorption (cm^{-1})	Absorption peaks of CCAC$_{L.A}$ after Adsorption (cm^{-1})
-OH stretching of the alcohol group	3550.7 - 3761.8	3535.8 - 3779.7	3511.2 - 3638.2	3500.6 - 37634.2
-NH stretching of the amine group	3286.5 - 3448.7	3225.3 - 3481.5	3229.3 - 3458.3	3287.9 - 3443.0
C-H asymmetric stretching of alkene group	3025.6 - 3117.1	3033.4 - 3159.9	3005.0 - 3108.1	3096.3
C-H symmetric stretching of alkane group	2917.5 - 2973.6	2911.3 - 2950.6	2865.3 - 2953.4	2929.7 - 2995.9
-OH stretching of the carboxylic acid group	2486.4 - 2797.0	2453.6 - 2753.3	2525.3 - 2773.0	2533.8 - 2795.2
C≡C stretching of the alkyne group	2071.2 - 2280.1	2049.6 - 2297.8	2064.2 - 2164.9	2054.2 - 2257.0
C=O stretching of the carbonyl group	1642.9 - 1932.8	1609.3 - 1947.8	1600.8 - 1732.1	1654.5 - 1732.8
C=C stretching of aromatic benzene ring group	1481.6 - 1592.1	1393.0 - 1530.1	1483.9 - 1567.2	1504.7 - 1582.3
C-O stretching of the alcohol group	1050.2 - 1236.2	1011.1 - 1295.2	1056.7 - 1192.9	1165.6 - 1228.2

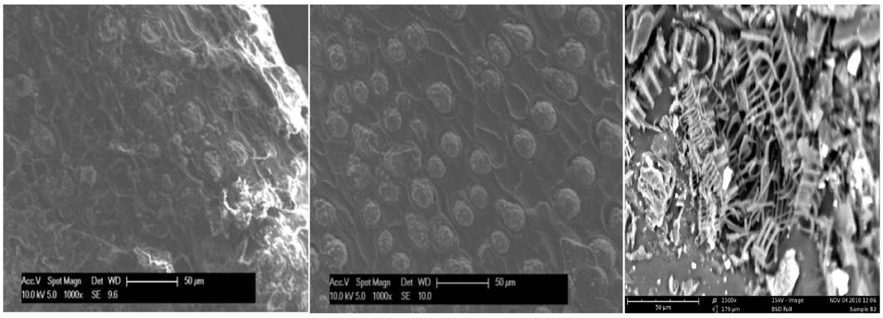
3.3. Surface Morphology Analysis of the Adsorbent

The surface morphology of raw empty palm fruit bunch, raw coconut coir, pre-treated empty palm fruit bunch and pre-treated coconut coir activated carbon material surfaces were examined by SEM and the images of the adsorbent showed highly irregular size and shape as illustrated in Figures 1(a)-(c) and Figures 2(a)-(c). Based on Figure 1(a), the raw coconut coir exhibited distinctive morphological features, including small pores and rod-like structures with uneven porosity and irregular sizes.



(a) (b) (c)

Figure 1. SEM photographs of (a) raw coconut coir before chemical activation. Magnification: 10,000×; HV: 500 KV; WD: 5.5 mm; Spot: 3.0; Det: LVD; ITMA: 10 µm. SEM photographs of activation (b) pre-treated coconut coir after chemical activation. Magnification: 10,000×; HV: 500 KV; WD: 5.2 mm; Spot: 3.0; Det: LVD; ITMA: 10 µm. (c) SEM photographs of (c) pre-treated $\text{CCAC}_{\text{L.A}}$ after adsorption. Magnification: 10,000×; HV: 15 KV-image; BSD Full; 208 µm; ITMA: 80 µm.



(a) (b) (c)

Figure 2. SEM photographs of (a) raw palm fruit bunch before chemical activation. Magnification: 1000×; HV: 10 KW; WD: 9.6 mm; Spot: 5.0; Det: SE; ITMA: 10 µm. SEM photographs of (b) pre-treated empty palm fruit bunch after chemical activation. Magnification: 1000×; HV: 10.0 KV; WD: 10.0 mm; Spot: 5.0; Det: SE; ITMA: 50 µm. SEM photographs of (c) pre-treated $\text{EPFB}_{\text{L.A}}$ after adsorption. Magnification: 1500×; HV: 15 KV-image; BSD Full; 179 µm; ITMA: 50 µm.

These characteristics suggested a complex and heterogeneous microstructure. The sharp edges observed on the rod-like structures further indicated that the raw coconut coir possesses good crystallinity, implying a well-ordered molecular arrangement within its fibrous composition. The raw empty palm fruit bunch (EPFB) sample in Figure 2(a) showed that the fibres were still bound to each other due to the presence of cuticle pores on the surface and had slightly smooth and flat surface due to the presence of wax which coats the surface of the fibre [48].

As seen in **Figures 1(a)-(c)** and **Figures 2(a)-(c)**, the surface morphology of untreated empty palm fruit bunch and coconut coir materials were different from the treated ones as the treatment significantly altered the physicochemical properties and porosity of the adsorbent materials and also; the treatment with lauric acid resulted in the partial removal of the protective thin wax layer on the adsorbent surface, as evidenced in **Figure 1(b)** and **Figure 2(b)**. This treatment also caused perforations due to the leaching of structural materials, which exposed the active sites on the adsorbent surface. Consequently, the perforations caused by the leaching of structural materials led to the creation of available pores and a large internal surface area on the adsorbent surface. This increased surface area and pore volume enhanced the adsorbent's capacity for adsorption, allowing it to bind and remove target molecules or substances more effectively [49] [50]. **Figure 1(c)** and **Figure 2(c)** demonstrated that after adsorption, both $EPFBAC_{L.A}$ and $CCAC_{L.A}$ exhibited uneven and irregular surfaces with significant rough, heterogeneous pores layers indicating that these structural characteristics provide a high potential for crude oil adsorption. The SEM images provided visual confirmation that the adsorbent surface features a porous structure with cracks and macro-pores. This porous architecture facilitated the easy diffusion of crude oil molecules into the pore structures and onto the surface of the adsorbent; thus, enhancing the adsorption process.

3.4. Factors Influencing the Batch Adsorption Equilibrium Studies

The batch adsorption equilibrium studies for the adsorption of crude oil onto $EPFB_{L.A}$ and $CCAC_{L.A}$ were investigated as follows.

3.4.1. Effect of Contact Time

The impact of contact time on crude oil adsorption onto EPFB and CCAC pre-treated with Lauric acid was observed across varying durations, with intervals of 5 minutes, spanning a total of 50 minutes. As illustrated in **Figure 3**, the initial adsorption onto $EPFB_{L.A}$ and $CCAC_{L.A}$ occurred rapidly within the first 5 - 15 minutes, gradually slowing down as the process advanced, ultimately reaching saturation at an equilibrium contact time of 45 - 50 minutes, respectively. This swift initial adsorption can be attributed to the significant concentration gradient between the adsorbate and the adsorbent's solid surface, along with the abundance of available active sites for adsorption [10]. However, as the process progressed, the rate of crude oil adsorption onto $EPFB_{L.A}$ and $CCAC_{L.A}$ decreased. This was due to the increased prominence of intra-particle diffusion, which led to higher mass transfer resistance for crude oil molecules moving from the adsorbent's surface to its internal adsorption sites [16] [51]. As the adsorption progressed towards equilibrium, the active sites on the adsorbent's surface gradually became saturated, leading to a corresponding decline in the adsorption rate [52]. $EPFB_{L.A}$ and $CCAC_{L.A}$ exhibited notable adsorption capacities of 1943.15 mg/g and 1943.85 mg/g, respectively, along with a high % removal of crude oil (99.96% and 99.99%, respectively).

This efficacy can be attributed to the ample availability of large surface areas (active sites) and a substantial solute concentration gradient conducive to crude oil adsorption. The process was further facilitated by rapid pore diffusion into the intra-spatial particle matrix, ultimately achieving equilibrium at 45 - 50 minutes. Consequently, there was a swift diffusion onto the external surface of the adsorbents [11] [53].

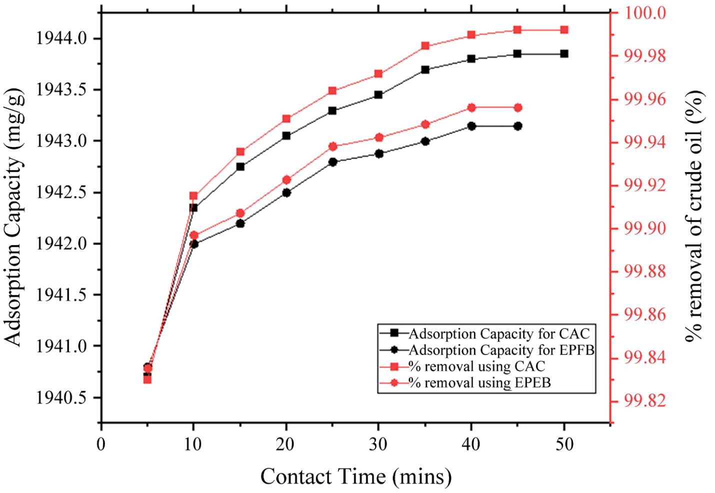


Figure 3. The influence of contact time on the adsorption of crude oil onto $EPFB_{L.A}$ and $CCAC_{L.A}$.

3.4.2. Effect of Adsorbent Dosage

The impact of adsorbent dosage on crude oil adsorption onto EPFB and CCAC pre-treated with Lauric acid was investigated by varying the dosage from 2.2 g to 3.0 g. As depicted in **Figure 4**, the % removal of crude oil exhibited an immediate increase with rising adsorbent dosage, reaching equilibrium at 99.93% and

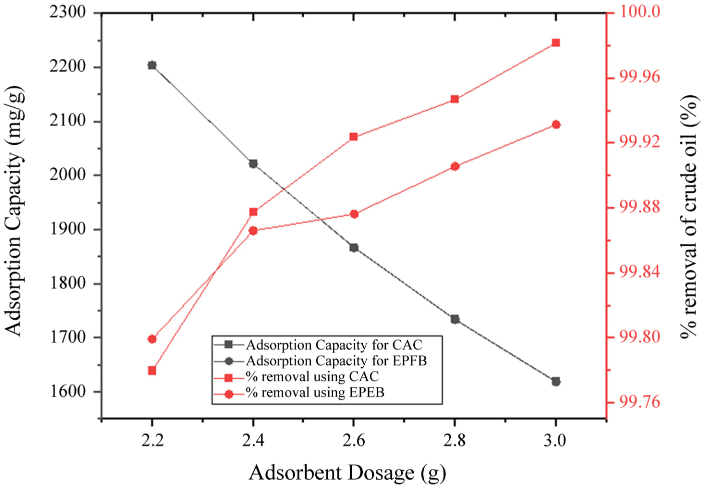


Figure 4. The influence of adsorbent dosage on the adsorption of crude oil onto $EPFB_{L.A}$ and $CCAC_{L.A}$.

99.98% for $EPFB_{L.A}$ and $CCAC_{L.A}$, respectively. This phenomenon can be attributed to the augmented surface area, pores, active sites, and the number of unsaturated sites available for adsorption [54].

In contrast, the adsorption capacity demonstrated a decrease with escalating adsorbent dosage. The maximum adsorption capacities of 2204.659 mg/g and 2204.227 mg/g were achieved when 2.2 g of $EPFB_{L.A}$ and $CCAC_{L.A}$ were utilized, respectively. This decline in adsorption capacity can be attributed to the increase in adsorbent dosage, leading to more active sites available for the adsorption process. Since there was a constant amount of crude oil to be adsorbed, the rise in active sites resulted in an enhanced percentage removal of crude oil [55].

3.4.3. Effect of Initial Crude Oil Concentration

The impact of initial crude oil concentration on crude oil adsorption onto EPFB and CCAC pre-treated with lauric acid, as depicted in **Figure 5**, revealed that an increase in the initial crude oil concentration augmented the adsorption capacity. However, this escalation also resulted in a diminished% removal of crude oil from $EPFB_{L.A}$ and $CCAC_{L.A}$. This indicates that while the adsorbents could take up more crude oil at higher concentrations, the efficiency of the adsorption process decreased due to the saturation of available adsorption sites. This decline in the % removal can be attributed to the insufficient availability of active sites on the adsorbent for crude oil adsorption beyond a certain concentration threshold. These active sites became saturated, leading to a plateau in adsorption efficiency. With further increases in crude oil concentration, no additional adsorption occurred, resulting in crude oil remaining in the final solution [56].

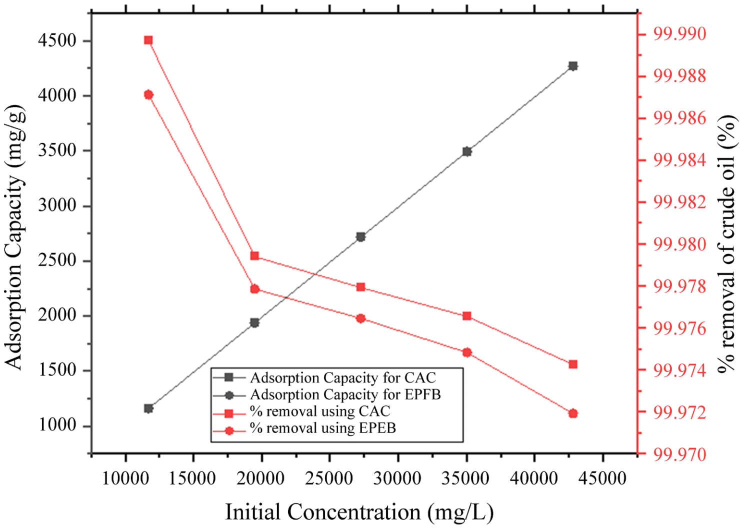


Figure 5. The influence of initial crude oil concentration on the adsorption of crude oil onto $EPFB_{L.A}$ and $CCAC_{L.A}$.

3.4.4. Effect of Agitation Speed

The influence of agitation speed on the adsorption of crude oil onto $EPFBAC_{L.A}$ and $CCAC_{L.A}$ was explored within the range of 20 - 100 rpm for 60 minutes.

Figure 6 illustrates that elevating the agitation speed correlated with higher adsorption capacity and percentage removal of crude oil. This observation validated the notion that heightened agitation speed enhanced the rate of mass transfer; thus, reducing surface-oil film resistance. Consequently, residual crude oil can more readily access the surface of the activated carbon [57]. At 100 rpm, the maximum sorption was attained, yielding an adsorption capacity of 1943.72 mg/g and 1943.67 mg/g, with a corresponding % removal of crude oil of 99.99% and 99.98% when utilizing 2.5 g of EPFBAC$_{\text{L.A}}$ and CCAC$_{\text{L.A}}$, respectively.

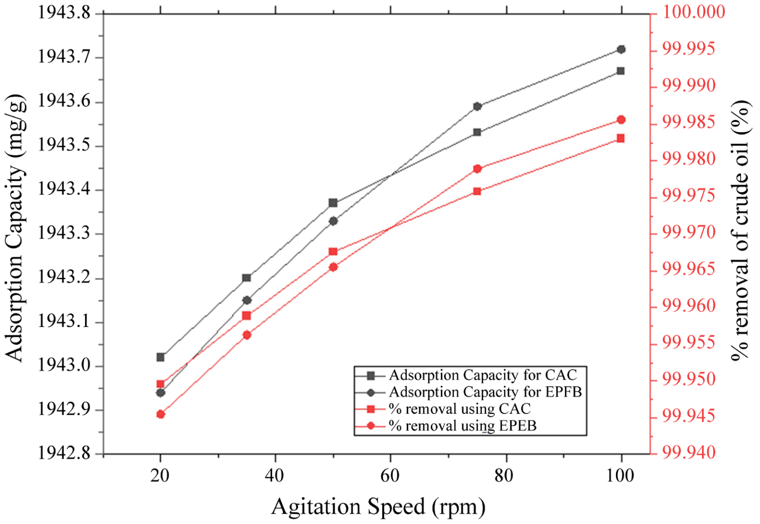


Figure 6. The influence of agitation speed on the adsorption of crude oil onto EPFB$_{\text{L.A}}$ and CCAC$_{\text{L.A}}$.

3.4.5. Effect of Temperature

The impact of temperature on crude oil adsorption onto CCAC pre-treated with Lauric acid was examined across various temperatures, as illustrated in **Figure 7**. Notably, with increasing temperature, there was a concurrent rise in both adsorption capacity and percentage removal of crude oil. The maximum sorption was achieved at 31˚C, yielding adsorption capacities of 1943.82 mg/g and 1943.28 mg/g, along with percentage removals of crude oil of 99.99% and 99.96% for EPFB$_{\text{L.A}}$ and CCAC$_{\text{L.A}}$, respectively.

This temperature-dependent enhancement in % removal of crude oil can be attributed to several factors. Firstly, the increase in kinetic forces and the weakening of hydrogen bonds and Vander Waals forces at higher temperatures strengthened the physical interaction between crude oil molecules and adsorbent active sites [9]. Additionally, chemical interactions between the adsorbents and adsorbate, the creation of new adsorption sites, or accelerated intra-particle diffusion of adsorbate species into the pores of activated adsorbents may occur at higher temperatures [58]. Moreso, increasing the temperature enhanced the diffusion rate of crude oil molecules across the external boundary layer and into the internal pores of the adsorbent particles. This enhancement in diffusion is attributed to the decreased solution viscosity and the increased solubility of crude oil in water at higher temperatures [59]. This inverse relationship between oil viscosity and penetration rate into the adsorbent interior surfaces further accentuates the impact of temperature. Notably, the temperature range of 23˚C to 31˚C chosen for the batch adsorption experiment corresponds to the sea surface temperature (SST) within the Niger Delta region of Nigeria. This selection ensured that the experimental conditions closely mimic the natural environmental conditions of the area; thus, enhancing the relevance and applicability of the findings to real-world scenarios in this region [60].

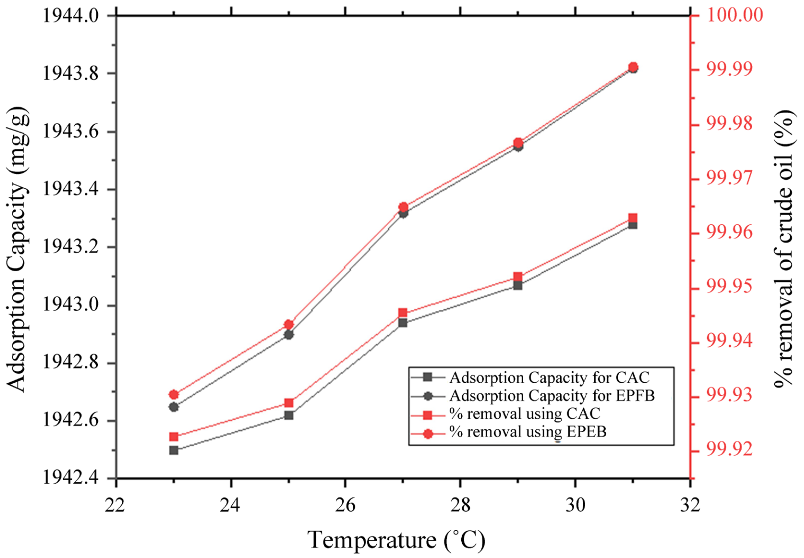


Figure 7. The influence of temperature on the adsorption of crude oil onto EPFB$_{L.A}$ and CCAC$_{L.A}$.

3.4.6. Effect of Particle Size

The impact of particle size on crude oil adsorption onto EPFB and CCAC pre-treated with Lauric acid was explored across varying particle sizes, as depicted in **Figure 8**. Notably, an increase in particle size correlated with a simultaneous increase in both adsorption capacity and percentage removal of crude oil. The maximum sorption was attained at a particle size of 500 μm, yielding adsorption capacities of 1943.08 mg/g and 1943.53 mg/g, along with percentage removals of crude oil of 99.95% and 99.98% for EPFB$_{L.A}$ and CCAC$_{L.A}$, respectively.

Figure 8 illustrates that as the particle size increased, both the adsorption capacity and% removal of crude oil increased accordingly. This observation supports the notion that the adsorption capacity rises as the surface area of the adsorbent decreases where larger particles of adsorbents possess a larger surface area, facilitating interstitial packing and promoting a faster rate of adsorption. This is due to the increased volume-to-surface-area ratio and the resulting enhanced surface area available for adsorption. The interstitial packing of larger particles provided additional sites for adsorption, leading to a faster rate of adsorption and higher adsorption capacity. Thus, this confirms that particle size distribution influences both adsorption capacity and the rate of adsorption [16].

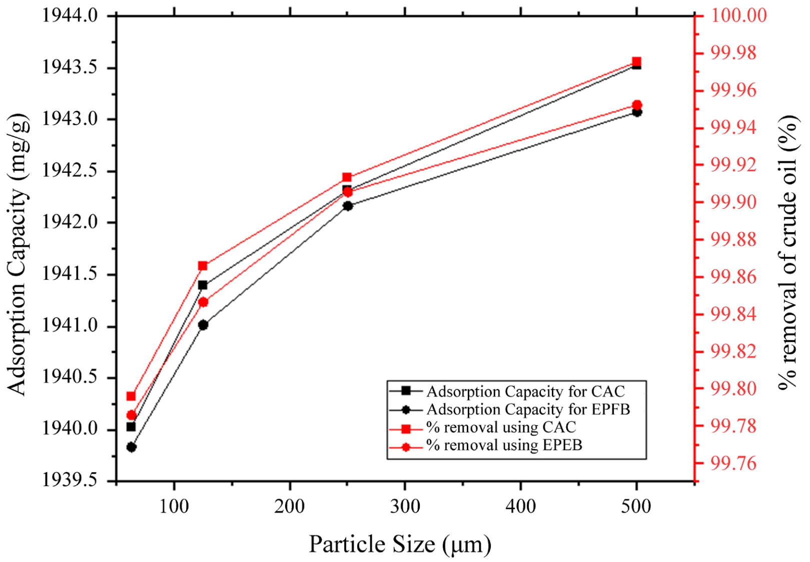


Figure 8. The influence of particle size on the adsorption of crude oil onto EPFB$_{L.A}$ and CCAC$_{L.A}$.

3.5. Batch Adsorption Isotherm

The adsorption isotherms, which are essential for studying the interaction between the adsorbent and adsorbate, were analysed using plots of the adsorption capacity of crude oil at equilibrium (q_e) versus the equilibrium concentration of crude oil (C_e). Figure 9 and Figure 10 depict these isotherms for crude oil adsorption onto EPFBAC$_{L.A}$ and CCAC$_{L.A}$, respectively. Five isotherm models were applied: Langmuir, Freundlich, Temkin, Toth, and Redlich-Peterson models and the suitability of these isotherm equations in describing the adsorption process was evaluated based on correlation coefficient (R^2) values. Figure 9 showed that the Freundlich isotherm model yielded the highest adsorption capacity of 4264.082 mg/g for EPFBAC$_{L.A}$, followed by the Redlich-Peterson, Toth, and Langmuir models. In contrast, the Temkin model was found to have the least adsorption capacity of 3901.258 mg/g. This indicates that the Freundlich model best describes the adsorption process for EPFBAC$_{L.A}$, suggesting multilayer adsorption on a heterogeneous surface.

In contrast, the Redlich-Peterson model was observed to have the highest adsorption capacity of 4219.194 mg/g for CCAC$_{L.A}$, followed by the Sip, Toth, Freundlich and Langmuir model but the Temkin model was found to have the least adsorption capacity of 3829.936 mg/g as shown in Figure 10. Hence, this result validates the suitability of two and three-parameter models in analysing the adsorption isotherm studies.

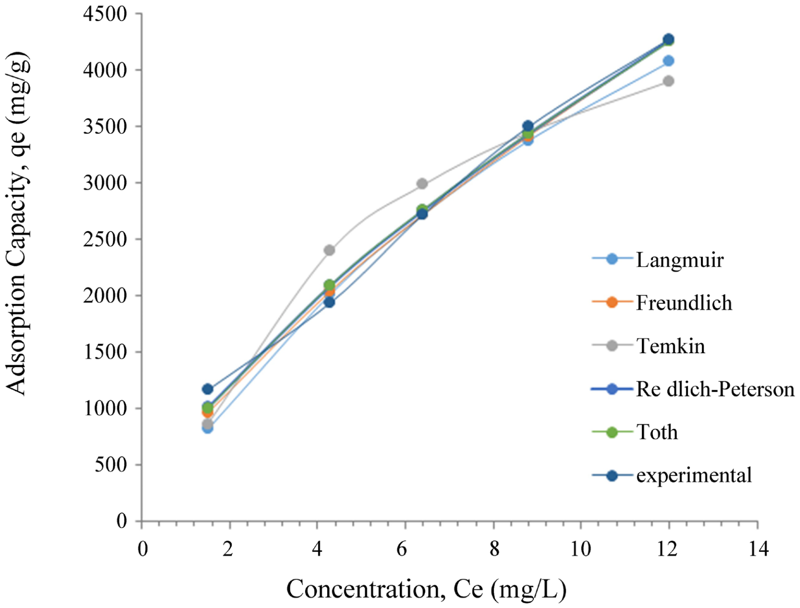


Figure 9. Isotherm plots for the adsorption of crude oil onto $EPFBAC_{L.A}$.

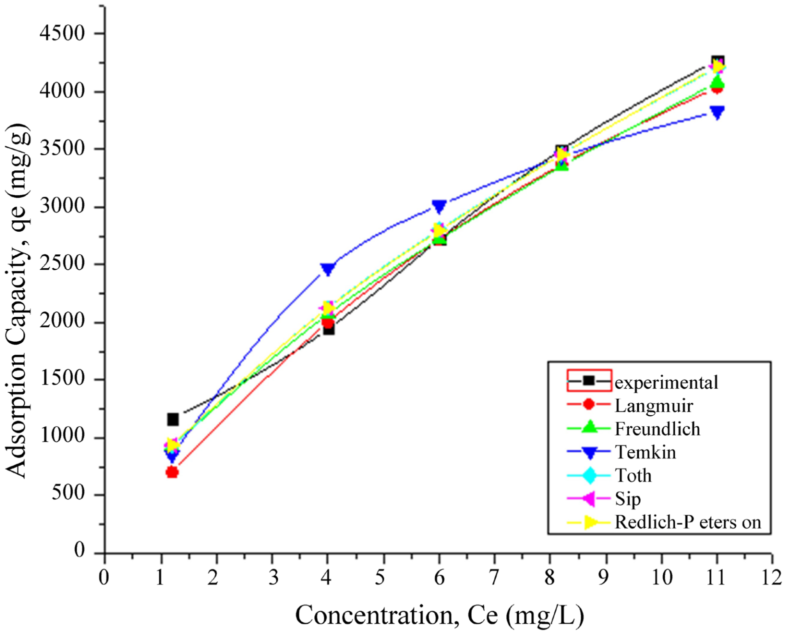


Figure 10. Isotherm plots for the adsorption of crude oil onto $CCAC_{L.A}$.

Table 3 showed that the Freundlich isotherm model had the best fit to the experimental data with an R^2 value of 1.00 and 1.00 for $EPFBAC_{L.A}$ and $CCAC_{L.A}$ respectively which suggested that the crude oil adsorption progressed from a multilayer adsorption process to a homogeneous process. Thus, the multilayer process contributed to the monolayer adsorption mechanism of crude oil adsorption from oil spillage by both $EPFBAC_{L.A}$ and $CCAC_{L.A}$ and also suggested that alkaline-based chemical activation enhanced the process of crude oil adsorption onto the adsorbent surfaces by providing more hydrophobic reactive sites [61]. The K_f value was 7.22 × 10^2 mg/g and 8.20 × 10^2 mg/g for $EPFBAC_{L.A}$ and $CCAC_{L.A}$ respectively indicating that as the K_f value increased, the adsorption capacity of both $EPFBAC_{L.A}$ and $CCAC_{L.A}$ also increased.

Table 3. Adsorption Isotherm constant for the removal of crude oil using $EPFBAC_{L.A}$ and $CCAC_{L.A}$.

Adsorbents	Adsorption Isotherm Models											
	Langmuir		Freundlich		Temkin		Toth		Sip		Redlich-Peterson	
$EPFBAC_{L.A}$	q_m (mg/g)	9.42 × 10^3	K_f (mg/g)	7.22 × 10^2	A (L/g)	1.2077	q_m (mg/g)	2.11 × 10^{10}	q_{ms} (mg/g)	-	A	5.1 × 10^5
	K_L (L/mg)	0.0635	N	1.40	B	1.6988	KT (L/mg)	0.392273	a_s (L/g)	-	B	6.7 × 10^2
							T	0.07385	B_s	-	B	0.308204
	R^2	1.000	R^2	1.000	R^2	0.922	R^2	0.9906	R^2	-	R^2	0.9914
$CCAC_{L.A}$	q_m (mg/g)	9.66 × 10^3	K_f (mg/g)	8.20 × 10^2	A (L/g)	1.5724	q_m (mg/g)	1.98 × 10^{10}	q_{ms} (mg/g)	4.33 × 10^7	A	5.309 × 10^5
	K_L (L/mg)	0.0654	N	1.49	B	1.34 × 10^3	K_T (L/mg)	0.42117	a_s (L/g)	1.92 × 10^{-5}	B	6.395 × 10^2
							T	0.07152	B_s	0.6786	B	0.3217
	R^2	1.000	R^2	1.000	R^2	0.9010	R^2	0.983	R^2	0.9845	R^2	0.9845

According to Liu *et al.* (2010) [62], adsorption is considered favourable when ($1 < n < 10$), and a higher (n) value indicates stronger adsorption intensity. In this study, the (n) values were greater than unity ($n = 1.40$) and ($n = 1.49$), indicating that the crude oil was favourably adsorbed on both $EPFBAC_{L.A}$ and $CCAC_{L.A}$, respectively. This suggests strong adsorption interactions between the adsorbents and the crude oil. Similar results were reported on crude oil sorption by cotton fibres, rice husks (acetylated and unacetylated) and thermally treated rice husks, respectively [47] [52] [56].

3.6. Batch Adsorption Kinetics

Several kinetic models such as the pseudo-first order, pseudo-second order, intra-particle diffusion and Boyd models were used to analyse the kinetic behaviour and mechanism of crude oil adsorption onto $EPFBAC_{L.A}$ and $CCAC_{L.A}$ which further provided insights into the adsorption process and the role of different forces in the sorption mechanism. The adsorption kinetic model constants for the removal of crude oil are shown in **Table 4** which demonstrates the coefficient of correlation (R^2) for the pseudo-second-order kinetic model for both $EPFBAC_{L.A}$ ($R^2 = 0.970$) and $CCAC_{L.A}$ ($R^2 = 0.983$) was much higher and closer to unity compared to that of the pseudo-first-order kinetic model and intraparticle diffusion models. This indicates that the pseudo-second-order kinetic model provides a better fit to the experimental data, suggesting that the adsorption process is likely governed by chemisorption mechanisms rather than physical adsorption. The pseudo-second-order kinetic model suggested that the rates of surface reaction and chemical reaction (chemisorption) were predominant in the crude oil adsorption process onto EPFBAC$_{L.A}$ and CCAC$_{L.A}$. This was likely facilitated by the high hydrophobic nature of the modified adsorbents, which enhanced the affinity of the adsorbents for the hydrophobic crude oil molecules. The faster rates of transport of crude oil from the liquid phase to the adsorbent phase further support the efficient removal of crude oil by these modified adsorbents [61] [63]. The observation that the intraparticle diffusion model had a greater contribution to surface sorption, as indicated by the large intercept (boundary layer effect; C), suggests that while chemisorption may dominate the overall adsorption process, the rate-controlling step could still be influenced by intra-particle diffusion. This indicates that even though chemisorption reactions occur rapidly on the surface of the adsorbents, the diffusion of crude oil molecules within the adsorbent particles may still play a significant role in determining the overall rate of adsorption. Therefore, both surface sorption and intra-particle diffusion contribute to the complex kinetics of crude oil adsorption onto EPFBAC$_{L.A}$ and CCAC$_{L.A}$ [64]. The coefficient of correlation and the thickness of the boundary layer for both EPFBAC$_{L.A}$ ($R^2 = 0.9064$; C = 1940.205) and CCAC$_{L.A}$ ($R^2 = 0.8776$; C = 1944.043) indeed validates the presence of some degree of boundary layer control in the adsorption process. This suggested that while intra-particle diffusion plays a significant role, it was not the sole rate-limiting step. Other processes, such as surface reaction kinetics and mass transfer limitations at the liquid-solid interface, might have also influenced the overall rate of adsorption. Therefore, a combination of factors, including both intra-particle diffusion and boundary layer effects, contributed to the observed kinetics of crude oil adsorption onto EPFBAC$_{L.A}$ and CCAC$_{L.A}$ [65].

Table 4. Adsorption kinetic model constants for the removal of crude oil using CCAC$_{KOH}$.

		Pseudo-first order			**Pseudo-second order**			**Intra-particle Diffusion**			
Adsorbents	$q_{e,exp}$ (mg/g)	K_f (g/mg·min)	$q_{e,cal}$ (mg/g)	R^2	K_s (g/mg·min)	$q_{e,cal}$ (mg/g)	R^2	K_{ip} (mg/g·min$^{1/2}$)	C (mg/g)	$q_{e,cal}$ (mg/g)	R^2
EPFBAC$_{L.A}$	1943.15	1.3847	1942.71	0.7763	0.0768	1943.316	0.970	0.4781	1940.205	1942.498	0.9064
CCAC$_{L.A}$	1943.85	1.3199	1943.34	0.790	0.05715	1944.104	0.983	0.57207	1940.21	1944.043	0.8776

The linearity test of the plot of B_t against time was used to distinguish between the film and particle-diffusion controlled adsorption mechanism as shown in **Figure 11** and **Figure 12**.

According to Bulut *et al.* 2008 [66], which stated that if the plot is a straight line passing through the origin, the adsorption rate is governed by particle diffusion; otherwise, it is governed by film diffusion. In the context of this study, the observed deviation from a straight line passing through the origin in the intra-particle diffusion plots suggests that film diffusion, rather than particle diffusion, may have contributed to the overall adsorption rate. This deviation could arise from variations in the mass transfer rate during different stages of the adsorption process, highlighting the dynamic nature of the adsorption phenomena

[67]. **Figure 11** and **Figure 12** showed the linear Boyd model plots for crude oil adsorption onto $EPFBAC_{L.A}$ and $CCAC_{L.A}$ respectively, did not pass through the origin, confirming that the adsorption mechanism was film-diffusion controlled; thus, highlighting the importance of external mass transfer resistance in these adsorption processes and in designing and optimizing the adsorption systems for crude oil removal. Similar results were reported indicating that the adsorption kinetics followed a pseudo-second-order model with the intra-particle diffusion and Boyd model confirming that the intra-particle and film-diffusion controlled mechanism occurred through the internal transport diffusion mechanism [44] [53] [61] [68].

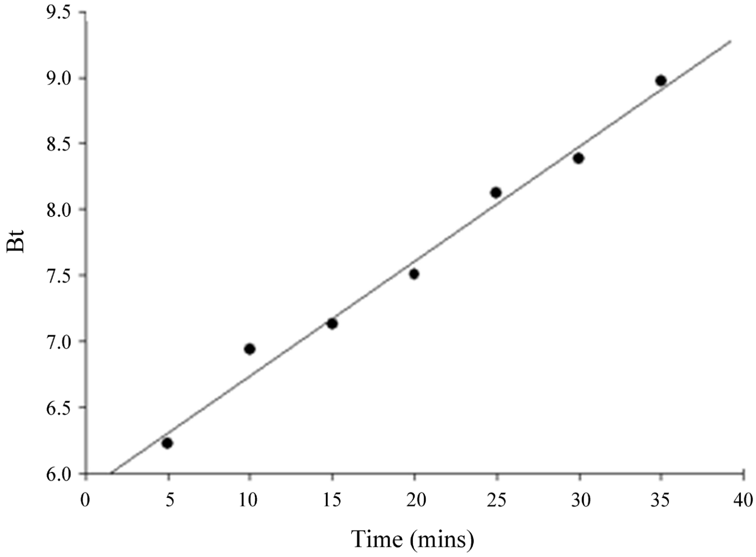


Figure 11. Boyd model plot for the adsorption of crude oil onto $EPFBAC_{L.A}$.

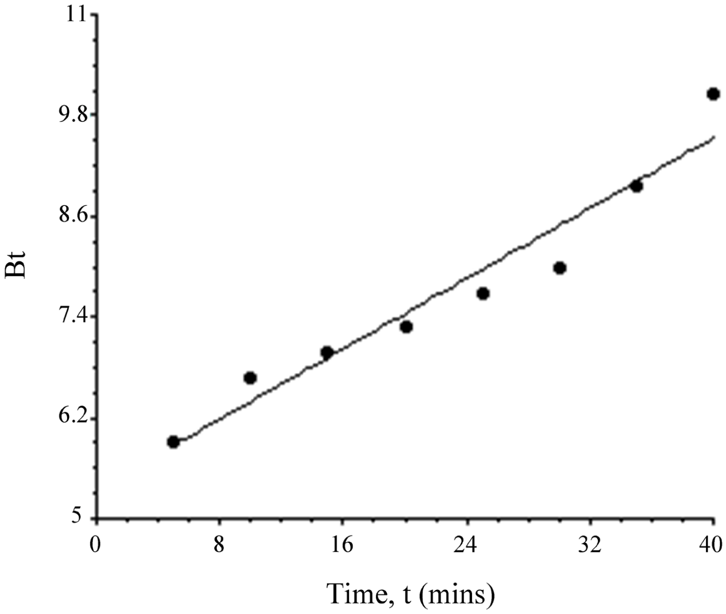


Figure 12. Boyd model plot for the adsorption of crude oil onto $CCAC_{L.A}$.

3.7. Thermodynamic Studies

The thermodynamics parameters were evaluated to confirm the nature of the adsorption.

The effect of temperature on the adsorption of crude oil onto EPFBAC$_{L.A}$ and CCAC$_{L.A}$ were evaluated over the temperature range of 296 - 304 K. The adsorption capacity and percentage removal of crude oil increased with an increase in temperature, as shown in **Table 5** and **Table 6**, respectively. This indicates that the process was endothermic, meaning it required energy input to proceed.

The thermodynamic parameters were determined at different temperatures for EPFBAC$_{L.A}$ and CCAC$_{L.A}$ are listed in **Table 5** and **Table 6**, respectively.

Table 5. Thermodynamics studies on the removal of crude oil using EPFBAC$_{L.A}$.

Temperature (K)	q_e (mg/g)	% Removal of crude oil	ΔG^o (KJ/mol)	ΔHo (KJ/mol)	ΔS^o (KJ/mol·K)	E_a (KJ/mol)
296	1942.650	99.930	−17.890	183.890	0.680	183.889
298	1942.900	99.940	−18.520	183.890	0.680	183.889
300	1943.320	99.970	−19.850	183.890	0.680	183.889
302	1943.550	99.980	−21.020	183.890	0.680	183.889
304	1943.820	99.990	−23.470	183.890	0.680	183.889

Table 6. Thermodynamics studies on the removal of crude oil using CCAC$_{L.A}$.

Temperature (K)	q_e (mg/g)	% Removal of crude oil	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (KJ/mol·K)	E_a (KJ/mol)
296	1942.500	99.923	−17.636	69.656	0.295	69.656
298	1942.620	99.929	−17.636	69.656	0.295	69.656
300	1942.940	99.945	−17.636	69.656	0.295	69.656
302	1943.070	99.952	−17.636	69.656	0.295	69.656
304	1943.280	99.963	−17.636	69.656	0.295	69.656

The negative values of ΔG^o at different temperatures indicated that the adsorption was thermodynamically favourable, feasible and spontaneous; suggesting that the process was favoured under the given conditions which implied that the adsorption occurred naturally without the need for external energy input. A decrease in the ΔG^o values with increasing temperature indicated that the adsorption process was spontaneous and more favourable at lower temperatures [69]. The positive values of ΔH^o for both EPFBAC$_{L.A}$ (ΔH^o = 183.890 KJ/mol) and CCAC$_{L.A}$ (ΔH^o = 69.656 KJ/mol) implied that the adsorption reaction of crude oil was endothermic. The increase in adsorption capacity with temperature was a result of the increased rate of diffusion of crude oil molecules across the external boundary layer and the internal pores of the adsorbent particles. This was due to the decrease in the viscosity of the solution as the temperature increased, allowing the molecules to move more freely and interact with the adsorbent more effectively [70]. Furthermore, the increase in the% removal of crude oil and the adsorption capacity at higher temperatures is likely due to a combination of increased pore size distribution, enhanced kinetic forces leading to greater mobility of crude oil species, improved diffusion rates, reduced viscosity, and possible structural changes in the adsorbent which collectively contribute to more efficient and effective adsorption at elevated temperatures [9] [66]. It is validated that the magnitude of the enthalpy is said to be about 20 - 40 KJ/mol for physisorption and 60 - 400 KJ/mol for chemisorption [71]. Hence, the absolute magnitudes of enthalpy for the adsorption of crude oil onto $\text{EPFBAC}_{\text{L.A}}$ (183.890 kJ/mol) and $\text{CCAC}_{\text{L.A}}$ (69.656 kJ/mol) falls within the range associated with chemisorption suggesting that the adsorption of crude oil onto these adsorbents involves significant chemical bonding between the crude oil molecules and the adsorbent surfaces. This implies that the adsorption process was likely driven by strong chemical interactions rather than weak van der Waals forces typical of physisorption. The positive values of ΔS^o for both $\text{EPFBAC}_{\text{L.A}}$ (ΔS^o = 0.68 KJ/mol·K) and $\text{CCAC}_{\text{L.A}}$ (ΔS^o = 0.295 KJ/mol·K) indicated that there was an increase in disorderliness and randomness at the adsorbent-adsorbate interface during the adsorption of crude oil from water due to the highly ordered crude oil molecules in the hydrophobic layer of both $\text{EPFBAC}_{\text{L.A}}$ and $\text{CCAC}_{\text{L.A}}$ at adsorption equilibrium; thus resulting in a gain of more translational entropy [72]. These results demonstrate that the thermodynamic behaviours of an adsorption system are dependent on the type of adsorbent and adsorbate being investigated. It is also influenced by the particle size or physical form of the adsorbent, its physical properties and the surface functional groups of the adsorbent as well as the characteristics and nature of the adsorbate. Morrison *et al.* (2011) [73] defined activation energy, E_a, as the minimum kinetic energy needed by the adsorbate molecules to react with the active sites available on the surface of the adsorbent; hence, the large values of E_a for $\text{EPFBAC}_{\text{L.A}}$ (E_a = 183.889 KJ/mol) and $\text{CCAC}_{\text{L.A}}$ (E_a = 69.656 KJ/mol) showed the presence of a high energy barrier to initiate the reaction which also verified the adsorption of crude oil onto $\text{EPFBAC}_{\text{L.A}}$ and $\text{CCAC}_{\text{L.A}}$ is a chemical adsorption. This elucidated the fact that the values of E_a were consistent with the magnitude of the activation energy for chemical adsorption which is usually between 40 and 400 KJ/mol [74] [75]. These results were also consistent with the values of enthalpy in **Table 5** and **Table 6**, which indicated that the crude oil adsorption on $\text{EPFBAC}_{\text{L.A}}$ and $\text{CCAC}_{\text{L.A}}$ took place via chemical adsorption. These results demonstrate that the thermodynamic behaviours of an adsorption system are dependent on the type of adsorbent and adsorbate, the particle size or physical form of the adsorbent, its physical properties and the surface functional groups of the adsorbent as well as the characteristics and nature of the adsorbate.

4. Conclusion

The impact of crude oil exploration and operations across the globe has resulted in the high risk of oil spillage and the accompanying environmental hazards. The current remediation techniques that are widely used in oil spill response are the physical, chemical, thermal and biological method; where the use of mechanical recovery and/or sorbents to remove oil from surface waters is highly preferable. The modified adsorbents had a very high adsorption capacity and% removal of crude oil. The adsorption kinetic studies followed Pseudo-second order model and adsorption isotherm studies best fitted Freundlich model. The modification of the surface morphology was evidently showed in the FTIR and SEM analysis. The thermodynamic studies showed that the reaction was chemisorption and endothermic in nature.

Ethics Statement

This work does not involve the use animal or human subject.

CRediT Author Statements

Ukpong, Anwana Abel: Conceptualization, Methodology, Data Curation, Validation, Formal Analysis, Writing—Original Draft Preparation, Review and Editing; **Otu, Gabriel Ekanem**: Investigation, Resources, Writing—Original Draft Preparation; **Oboh, Innocent Oseribho**: Validation, Formal Analysis, Investigation, Resources, Supervision; **Uzono, Romokere Isotuk**: Formal Analysis, Investigation, Resources, Project Administration, Funding Acquisition. **Akwayo, Iniobong Job**: Formal Analysis, Investigation, Resources, Project Administration, Funding Acquisition. **Inyang, Udeme Ibanga**: Investigation, Resources, Project Administration, Funding Acquisition.

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Conflicts of Interest

The authors declare that they have no competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

References

[1] George, I.I., Nawawi, M.G.M., Mohd, Z.J. and Farah, B.S. (2024) Environmental Effects from Petroleum Product Transportation Spillage in Nigeria: A Critical Review. *Environmental Science and Pollution Research*, **13**, 1719-1747. https://doi.org/10.1007/s11356-023-31117-z

[2] Okon, O.G. (2017) Bioaccumulation of Heavy Metals in Cucurbita Maxima Duch. and *Telfairia occidentalis* Hook. F. Grown on Crude Oil Polluted Soil. *American Journal of Agricultural Science*, **4**, 88-93.

[3] Egbe, R.E. (2010) Environmental Challenges of Oil Spillage for Families in Oil Producing Communities of the Niger Delta Region. *International Journal of Modern Engineering Research*, **3**, 3336-3342.

[4] Nwilo, P.C. and Badejo, O.T. (2005) Oil Spill Problems and Management in the Niger Delta. *International Oil Spill Conference Proceedings*, **2005**, 567-570. https://doi.org/10.7901/2169-3358-2005-1-567

[5] Polka, M., Bozena, K., Marek, W. and Joanne, R. (2015) Efficiency Analysis of the Sorbents Used to Adsorb the Vapours of Petroleum Products during Rescue and Fire-Fighting Asctions Przem. *Chemistry Journal*, **1**, 109-113. https://doi.org/10.15199/62.2015.3.13

[6] Ahmad, A.A., Hameed, B.H. and Aziz, N. (2007) Adsorption of Direct Dye on Palm Ash: Kinetic and Equilibrium Modeling. *Journal of Hazardous Materials*, **141**, 70-76. https://doi.org/10.1016/j.jhazmat.2006.06.094

[7] Chakraborty, S., De, S., DasGupta, S. and Basu, J.K. (2005) Adsorption Study for the Removal of a Basic Dye: Experimental and Modeling. *Chemosphere*, **58**, 1079-1086. https://doi.org/10.1016/j.chemosphere.2004.09.066

[8] Bhatnagar, A. and Sillanpää, M. (2010) Utilization of Agro-Industrial and Municipal Waste Materials as Potential Adsorbents for Water Treatment—A Review. *Chemical Engineering Journal*, **157**, 277-296. https://doi.org/10.1016/j.cej.2010.01.007

[9] Senthilkumaar, S., Kalaamani, P. and Subburaam, C. (2006) Liquid Phase Adsorption of Crystal Violet onto Activated Carbons Derived from Male Flowers of Coconut Tree. *Journal of Hazardous Materials*, **136**, 800-808. https://doi.org/10.1016/j.jhazmat.2006.01.045

[10] Ukpong, A.A., Asuquo, E.O. and Edekhe, G.I. (2023) The Adsorption Equilibrium and Kinetic Studies for the Removal of Crystal Violet Dye (Methyl Violet 6b) from Aqueous Solution Using Avocado Pear Seed Activated Carbon. *International Journal of Research and Scientific Innovation*, **X**, 154-164. https://doi.org/10.51244/ijrsi.2023.10419

[11] Ukpong, A.A., Edekhe, G.I. and Asuquo, E.O. (2024) The Adsorption Studies for the Removal of Lead (Pb2+) from Paint Industrial Wastewater Using Avocado Seed Activated Carbon (ASAC). *International Journal of Research and Scientific Innovation*, **XI**, 414-425. https://doi.org/10.51244/ijrsi.2024.1101032

[12] Tunde Folorunsho, A. (2016) A Statistical Approach to Optimization of Congo Red Dye Removal (CRDR) via Coconut Shell Activated Carbon (CSAC). *International Journal of Computational and Theoretical Chemistry*, **4**, 7-13. https://doi.org/10.11648/j.ijctc.20160402.11

[13] Senthilkumaar, S., Kalaamani, P., Porkodi, K., Varadarajan, P.R. and Subburaam, C.V. (2006) Adsorption of Dissolved Reactive Red Dye from Aqueous Phase onto Activated Carbon Prepared from Agricultural Waste. *Bioresource Technology*, **97**, 1618-1625. https://doi.org/10.1016/j.biortech.2005.08.001

[14] Kalavathy, M.H., Karthikeyan, T., Rajgopal, S. and Miranda, L.R. (2005) Kinetic and Isotherm Studies of Cu(II) Adsorption onto H_3PO_4-Activated Rubber Wood Sawdust. *Journal of Colloid and Interface Science*, **292**, 354-362. https://doi.org/10.1016/j.jcis.2005.05.087

[15] Tseng, R., Tseng, S. and Wu, F. (2006) Preparation of High Surface Area Carbons from Corncob with KOH Etching Plus CO_2 Gasification for the Adsorption of Dyes and Phenols from Water. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **279**, 69-78. https://doi.org/10.1016/j.colsurfa.2005.12.042

[16] Anwana Abel, U., Rhoda Habor, G. and Innocent Oseribho, O. (2020) Adsorption Studies of Oil Spill Clean-Up Using Coconut Coir Activated Carbon (CCAC). *American Journal of Chemical Engineering*, **8**, 36-47.

https://doi.org/10.11648/j.ajche.20200802.11

[17] Almeida-Naranjo, C.E., Gallegos, E., Domínguez, E., Gutiérrez, P., Valle, V., Aguilar, A.D., *et al.* (2023) From Renewable Biomass to Water Purification Systems: Oil Palm Empty Fruit Bunch as Bio-Adsorbent for Domestic Wastewater Remediation and Methylene Blue Removal. *Water*, **15**, Article 4116. https://doi.org/10.3390/w15234116

[18] Puasa, N.A., Ahmad, S.A., Zakaria, N.N., Shaharuddin, N.A., Khalil, K.A., Azmi, A.A., *et al.* (2022) Utilisation of Oil Palm's Empty Fruit Bunch Spikelets for Oil-Spill Removal. *Agronomy*, **12**, Article 535. https://doi.org/10.3390/agronomy12020535

[19] Hameed, B., Din, A. and Ahmad, A. (2007) Adsorption of Methylene Blue onto Bamboo-Based Activated Carbon: Kinetics and Equilibrium Studies. *Journal of Hazardous Materials*, **141**, 819-825. https://doi.org/10.1016/j.jhazmat.2006.07.049

[20] Tan, I.A.W., Hameed, B.H. and Ahmad, A.L. (2007) Equilibrium and Kinetic Studies on Basic Dye Adsorption by Oil Palm Fibre Activated Carbon. *Chemical Engineering Journal*, **127**, 111-119. https://doi.org/10.1016/j.cej.2006.09.010

[21] Awoh, E.T., Kiplagat, J., Kimutai, S.K. and Mecha, A.C. (2023) Current Trends in Palm Oil Waste Management: A Comparative Review of Cameroon and Malaysia. *Heliyon*, **9**, e21410. https://doi.org/10.1016/j.heliyon.2023.e21410

[22] Obada, D.O., Kekung, M.O., Levonyan, T. and Norval, G.W. (2023) Palm Oil Mill Derived Empty Palm Fruit Bunches as a Feed Stock for Renewable Energy Applications in Nigeria: A Review. *Bioresource Technology Reports*, **24**, Article ID: 101666. https://doi.org/10.1016/j.biteb.2023.101666

[23] Sunday Noah, A. (2022) Oil Palm Empty Fruit Bunches (OPEFB)—Alternative Fibre Source for Papermaking. In: Kamyab, H., Ed., *Elaeis guineensis*, IntechOpen, 5-6. https://doi.org/10.5772/intechopen.98256

[24] Sundalian, M., Larissa, D. and Suprijana, O. (2021) Contents and Utilization of Palm Oil Fruit Waste. *Biointerface Research in Applied Chemistry*, **3**, 10148-10160.

[25] Adepoju, T.F., Uzono, R.I. and Akwayo, I.J. (2017) Modelling and Optimization of the Removal of Congo-Red Dye from Waste Water Using Agricultural Waste. *Journal of Chemical, Environmental and Biological Engineering*, **1**, 1-7.

[26] Asadpour, R., Yavari, S., Kamyab, H., Ashokkumar, V., Chelliapan, S. and Yuzir, A. (2021) Study of Oil Sorption Behaviour of Esterified Oil Palm Empty Fruit Bunch (OPEFB) Fibre and Its Kinetics and Isotherm Studies. *Environmental Technology & Innovation*, **22**, Article ID: 101397. https://doi.org/10.1016/j.eti.2021.101397

[27] Puasa, N.A., Ahmad, S.A., Zakaria, N.N., Khalil, K.A., Taufik, S.H., Zulkharnain, A., *et al.* (2022) Oil Palm's Empty Fruit Bunch as a Sorbent Material in Filter System for Oil-Spill Clean Up. *Plants*, **11**, Article 127. https://doi.org/10.3390/plants11010127

[28] American Society of Testing and Materials (1991) Standard Test Methods for Moisture in Activated Carbon. ASTM, D 2867-91. ASTM Committee on Standards.

[29] American Society of Testing and Materials (1999) Standard Test Method for Volatile Content of Activated Carbon. ASTM, D 5832-98. ASTM Committee on Standards.

[30] American Society of Testing and Materials (1999) Standard Test Method for Ash Content of Activated Carbon. ASTM, D 2866-94. ASTM Committee on Standards.

[31] American Society of Testing and Materials (1999) Standard Test Method for Apparent Density of Activated Carbon. ASTM, D 2854-96. ASTM Committee on Standards.

[32] American Society for Testing and Materials (1996) Refractories, Carbon and

Graphic Products; Activated Carbon. ASTM, D 3838-80. Annual book of ASTM Standard, 15.01.

[33] Nwabanne, J.T. and Igbokwe, P.K. (2012) Application of Response Surface Methodology for Preparation of Activated Carbon from Palmyra Palm Nut. *New York Science Journal*, **5**, 18-25.

[34] Valix, M., Cheung, W.H. and McKay, G. (2004) Preparation of Activated Carbon Using Low Temperature Carbonisation and Physical Activation of High Ash Raw Bagasse for Acid Dye Adsorption. *Chemosphere*, **56**, 493-501. https://doi.org/10.1016/j.chemosphere.2004.04.004

[35] Maulina, S. and Iriansyah, M. (2018) Characteristics of Activated Carbon Resulted from Pyrolysis of the Oil Palm Fronds Powder. *IOP Conference Series: Materials Science and Engineering*, **309**, Article ID: 012072. https://doi.org/10.1088/1757-899x/309/1/012072

[36] Yakout, S.M. and Sharaf El-Deen, G. (2016) Characterization of Activated Carbon Prepared by Phosphoric Acid Activation of Olive Stones. *Arabian Journal of Chemistry*, **9**, S1155-S1162. https://doi.org/10.1016/j.arabjc.2011.12.002

[37] Thoe, J. M. L., Surugau, N. and Chong, H. L. H. (2019) Application of Oil Palm Empty Fruit Bunch as Adsorbent: A Review. *Transaction on Science and Technology*, **6**, 1-9.

[38] Pavan, F.A., Lima, E.C., Dias, S.L.P. and Mazzocato, A.C. (2008) Methylene Blue Biosorption from Aqueous Solutions by Yellow Passion Fruit Waste. *Journal of Hazardous Materials*, **150**, 703-712. https://doi.org/10.1016/j.jhazmat.2007.05.023

[39] Mopoung, S., Moonsri, P., Palas, W. and Khumpai, S. (2015) Characterization and Properties of Activated Carbon Prepared from Tamarind Seeds by KOH Activation for Fe(III) Adsorption from Aqueous Solution. *The Scientific World Journal*, **2015**, Article ID: 415961. https://doi.org/10.1155/2015/415961

[40] Adebajo, M.O. and Frost, R.L. (2004) Acetylation of Raw Cotton for Oil Spill Cleanup Application: An FTIR and 13C MAS NMR Spectroscopic Investigation. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **60**, 2315-2321. https://doi.org/10.1016/j.saa.2003.12.005

[41] Teas, C., Kalligeros, S., Zanikos, F., Stournas, S., Lois, E. and Anastopoulos, G. (2001) Investigation of the Effectiveness of Absorbent Materials in Oil Spills Clean Up. *Desalination*, **140**, 259-264. https://doi.org/10.1016/s0011-9164(01)00375-7

[42] Marín, A.B.P., Ortuño, J.F., Aguilar, M.I., Meseguer, V.F., Sáez, J. and Lloréns, M. (2010) Use of Chemical Modification to Determine the Binding of Cd(II), Zn(II) and Cr(III) Ions by Orange Waste. *Biochemical Engineering Journal*, **53**, 2-6. https://doi.org/10.1016/j.bej.2008.12.010

[43] Gong, R., Jin, Y., Chen, F., Chen, J. and Liu, Z. (2006) Enhanced Malachite Green Removal from Aqueous Solution by Citric Acid Modified Rice Straw. *Journal of Hazardous Materials*, **137**, 865-870. https://doi.org/10.1016/j.jhazmat.2006.03.010

[44] Sidik, S.M., Jalil, A.A., Triwahyono, S., Adam, S.H., Satar, M.A.H. and Hameed, B.H. (2012) Modified Oil Palm Leaves Adsorbent with Enhanced Hydrophobicity for Crude Oil Removal. *Chemical Engineering Journal*, **203**, 9-18. https://doi.org/10.1016/j.cej.2012.06.132

[45] Ibrahim, S., Wang, S. and Ang, H.M. (2010) Removal of Emulsified Oil from Oily Wastewater Using Agricultural Waste Barley Straw. *Biochemical Engineering Journal*, **49**, 78-83. https://doi.org/10.1016/j.bej.2009.11.013

[46] Ibrahim, S., Ang, H. and Wang, S. (2009) Removal of Emulsified Food and Mineral Oils from Wastewater Using Surfactant Modified Barley Straw. *Bioresource Tech-*

nology, **100**, 5744-5749. https://doi.org/10.1016/j.biortech.2009.06.070

[47] Kudaybergenov, K.K., Ongarbayev, E.K. and Mansurov, Z.A. (2012) Thermally Treated Rice Coirs for Petroleum Adsorption. *International Journal of Biological Chemistry*, **1**, 3-12.

[48] Wang, J., Zheng, Y. and Wang, A. (2012) Effect of Kapok Fiber Treated with Various Solvents on Oil Absorbency. *Industrial Crops and Products*, **40**, 178-184. https://doi.org/10.1016/j.indcrop.2012.03.002

[49] Fahma, F., Iwamoto, S., Hori, N., Iwata, T. and Takemura, A. (2010) Isolation, Preparation, and Characterization of Nanofibers from Oil Palm Empty-Fruit-Bunch (OPEFB). *Cellulose*, **17**, 977-985. https://doi.org/10.1007/s10570-010-9436-4

[50] Chung, S., Suidan, M.T. and Venosa, A.D. (2011) Partially Acetylated Sugarcane Bagasse for Wicking Oil from Contaminated Wetlands. *Chemical Engineering & Technology*, **34**, 1989-1996. https://doi.org/10.1002/ceat.201100353

[51] Olufemi, B.A. and Otolorin, F. (2017) Comparative Adsorption of Crude Oil Using Mango (*Mangnifera indica*) Shell and Mango Shell Activated Carbon. *Environmental Engineering Research*, **22**, 384-392. https://doi.org/10.4491/eer.2017.011

[52] Husseien, M., Amer, A.A., El-Maghraby, A. and Taha, N.A. (2008) Availability of Barley Straw Application on Oil Spill Clean Up. *International Journal of Environmental Science & Technology*, **6**, 123-130. https://doi.org/10.1007/bf03326066

[53] Elkady, M.F., Hussien, M. and Abou-rady, R. (2015) Equilibrium and Kinetics Behavior of Oil Spill Process onto Synthesized Nano-Activated Carbon. *American Journal of Applied Chemistry*, **3**, 22-30. https://doi.org/10.11648/j.ajac.s.2015030301.14

[54] Williams, N.E. and Nur, P.A. (2018) KOH Modified *Thevetia peruviana* Shell Activated Carbon for Sorption of Dimethoate from Aqueous Solution. *Journal of Environmental Science and Health*, **54**, 1-13.

[55] Itodo, H.U. and Itodo, A.U. (2010) Surface Coverage and Adsorption Study of Dye Uptake by Derived Acid and Base Treated Mango Seed Shells. *Journal of Chemical and Pharmaceutical Research*, **2**, 673-683.

[56] Thompson, N.E., Emmanuel, G.C., Adagadzu, K.J. and Yusuf, N.B. (2010) Sorption Studies of Crude Oil on Acetylated Rice Coirs. *Archives of Applied Science Research*, **2**, 142-151.

[57] Lin, C. and Liu, H. (1999) Adsorption in a Centrifugal Field: Basic Dye Adsorption by Activated Carbon. *Industrial & Engineering Chemistry Research*, **39**, 161-167. https://doi.org/10.1021/ie9902333

[58] Karthikeyan, T., Rajgopal, S. and Miranda, L. (2005) Chromium(VI) Adsorption from Aqueous Solution by Sawdust Activated Carbon. *Journal of Hazardous Materials*, **124**, 192-199. https://doi.org/10.1016/j.jhazmat.2005.05.003

[59] Li, J., Luo, M., Zhao, C., Li, C., Wang, W., Zu, Y., *et al.* (2013) Oil Removal from Water with Yellow Horn Shell Residues Treated by Ionic Liquid. *Bioresource Technology*, **128**, 673-678. https://doi.org/10.1016/j.biortech.2012.11.009

[60] Abowei, J.F.N. (2010) Salinity, Dissolved Oxygen, pH and Surface Water Temperature Conditions in Nkoro River, Niger Delta, Nigeria. *Advanced Journal of Food Science and Technology*, **2**, 36-40.

[61] Onwuka, J.C., Agbaji, E.B., Ajibola, V.O. and Okibe, F.G. (2018) Treatment of Crude Oil-Contaminated Water with Chemically Modified Natural Fiber. *Applied Water Science*, **8**, Article No. 86. https://doi.org/10.1007/s13201-018-0727-5

[62] Liu, Q., Zheng, T., Wang, P., Jiang, J. and Li, N. (2010) Adsorption Isotherm, Ki-

netic and Mechanism Studies of Some Substituted Phenols on Activated Carbon Fibers. *Chemical Engineering Journal*, **157**, 348-356. https://doi.org/10.1016/j.cej.2009.11.013

[63] Tan, I.A.W. and Hameed, B.H. (2010) Adsorption Isotherms, Kinetics, Thermodynamics and Desorption Studies of Basic Dye on Activated Carbon Derived from Oil Palm Empty Fruit Bunch. *Journal of Applied Sciences*, **10**, 2565-2571. https://doi.org/10.3923/jas.2010.2565.2571

[64] Eba, F., Gueu, S., Eya'A-Mvongbote, A., Ondo, J.A., Yao, B.K., Ndong, N.J. and Kouya, B.R. (2010) Evaluation of the Absorption Capacity of the Natural Clay from Bikougou (Gabon) to Remove Mn(II) from Aqueous Solution. *International Journal of Engineering and Science Technology*, **2**, 5001-5016.

[65] Srivastava, V.C., Swamy, M.M., Mall, I.D., Prasad, B. and Mishra, I.M. (2006) Adsorptive Removal of Phenol by Bagasse Fly Ash and Activated Carbon: Equilibrium, Kinetics and Thermodynamics. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **272**, 89-104. https://doi.org/10.1016/j.colsurfa.2005.07.016

[66] Bulut, Y. and Tez, Z. (2007) Removal of Heavy Metals from Aqueous Solution by Sawdust Adsorption. *Journal of Environmental Sciences*, **19**, 160-166. https://doi.org/10.1016/s1001-0742(07)60026-6

[67] Mohanty, K., Das, D. and Biswas, M.N. (2005) Adsorption of Phenol from Aqueous Solutions Using Activated Carbons Prepared from Tectona Grandis Sawdust by Zncl2 Activation. *Chemical Engineering Journal*, **115**, 121-131. https://doi.org/10.1016/j.cej.2005.09.016

[68] Ejikeme, P.C.N., Ejikeme, E.M. and Okonkwo, G.N. (2014) Equilibrium, Kinetic and Thermodynamic Studies on Basic Dye Adsorption Using Composite Activated Carbon. *International Journal of Technical Research and Applications*, **2**, 96-103.

[69] Auta, M. and Hameed, B.H. (2011) Preparation of Waste Tea Activated Carbon Using Potassium Acetate as an Activating Agent for Adsorption of Acid Blue 25 Dye. *Chemical Engineering Journal*, **171**, 502-509. https://doi.org/10.1016/j.cej.2011.04.017

[70] Jawad, A.H., Waheeb, A.S., Abd Rashid, R., Nawawi, W.I. and Yousif, E. (2018) Equilibrium Isotherms, Kinetics, and Thermodynamics Studies of Methylene Blue Adsorption on Pomegranate (*Punica granatum*) Peels as a Natural Low-Cost Biosorbent. *Desalination and Water Treatment*, **105**, 322-331. https://doi.org/10.5004/dwt.2018.22021

[71] Abidin, M.A.Z., Jalil, A.A., Triwahyono, S., Adam, S.H. and Nazirah Kamarudin, N.H. (2011) Recovery of Gold(III) from an Aqueous Solution onto a Durio Zibethinus Husk. *Biochemical Engineering Journal*, **54**, 124-131. https://doi.org/10.1016/j.bej.2011.02.010

[72] Gupta, V.K., Ganjali, M.R., Nayak, A., Bhushan, B. and Agarwal, S. (2012) Enhanced Heavy Metals Removal and Recovery by Mesoporous Adsorbent Prepared from Waste Rubber Tire. *Chemical Engineering Journal*, **197**, 330-342. https://doi.org/10.1016/j.cej.2012.04.104

[73] Morrison, R.T., Boyd, R.N. and Bhattacharjee, S.K. (2011) Organic Chemistry. 7th Edition, Pearson Education Inc.

[74] Fomkin, A. (2009) Nano-Porous Materials and Their Adsorption Properties. *Institute of Physical Chemistry and Electrochemistry. Russian Academy of Sciences*, **45**, 133-149.

[75] Li, Q., Chai, L., Yang, Z. and Wang, Q. (2009) Kinetics and Thermodynamics of Pb(II) Adsorption onto Modified Spent Grain from Aqueous Solutions. *Applied Surface Science*, **255**, 4298-4303. https://doi.org/10.1016/j.apsusc.2008.11.024