Synthesis of Activated Charcoal from Coconut Shell for the Removal of Crude Oil Spill

Mansur Yahaya Ibrahim [iD]; and Hafsat Adamu

Department of Pure and Industrial Chemistry, Sokoto State University, Sokoto.

Corresponding author: ymansur64@gmail.com

Abstract

Crude oil spills have devastating effects on the environment, particularly aquatic ecosystems. The purpose of the present research is to determine whether dry coconut shells can be used as raw materials to make activated charcoal (AC) via pyrolysis and whether they can be utilized as natural sorbents to clean up crude oil spills. The UV-Vis spectrum of the synthesized CSAC shows distinct peaks at 230 and 260 nm, whereas the activated charcoal exhibits peaks at 231 and 261 nm. The FTIR spectra of the synthesized CSAC reveal a medium broad absorption peak at 3307.2 cm^{-1}, while the raw coconut shell's FTIR spectra show a medium sharp peak at 2945.3 cm^{-1}. The SEM images highlight the unique structural properties of CSAC, showcasing high porosity, varied pore sizes, rough surface topography, and the presence of micropores and mesopores. The chemical activation significantly increased the hydrophobicity of the adsorbent, creating CSAC with a much better adsorption capacity for crude oil removal, having a maximum adsorption capacity of 4840.0 mg/g and the highest percentage of crude oil removal at 99.9985%, as proven by batch experiments for different adsorbent dosages. The batch experimental results indicated that the percentage of crude oil removal increased with an increase in adsorbent dosage and contact time. Based on the correlation coefficients (R^2) values (close to unity), it was generally observed that the plots match the Freundlich isotherm better than the Langmuir isotherm model. These findings have made the synthetic CSAC an attractive, useful, and environmentally friendly adsorbent.

Keywords: Crude Oil, Coconut Shell, Spill, Activated Charcoal, Pyrolysis, Adsorbent.

Introduction

The increasing frequency of crude oil spills caused by the exploration, production, transportation, storage, and consumption of petroleum oil poses significant environmental challenges, necessitating the development of effective remediation strategies. Among various methods for addressing oil pollution, adsorption has emerged as a promising technique due to its efficiency and cost-effectiveness. Activated charcoal, particularly that derived from coconut shells, has gained attention in recent years for its superior adsorption properties. This research paper explores the synthesis of activated charcoal from coconut shell biomass and its application in removing crude oil from contaminated water. (Bhardwaj et al., 2018, Adesanmi et al., 2021, Ordinioha and Brisibe, 2013)

Activated charcoal, also known as activated carbon, is a highly porous material with a large surface area and the ability to trap various substances through adsorption. It is widely recognized for its effectiveness in adsorbing organic compounds, including hydrocarbons present in crude oil. The effectiveness of activated charcoal in removing crude oil from contaminated environments can be attributed to its high adsorption capacity. The process of adsorption involves the adherence of molecules from a gas or liquid to a solid surface. In the case of crude oil spills, activated charcoal can adsorb hydrocarbons and other organic compounds present in the oil due to its porous structure and large surface area. This property allows it to trap contaminants effectively, thereby reducing their concentration in the environment. (Kusumaningtyas et al., 2019, Sahnoun and Boutahala, 2018)

Coconut shells are an abundant agricultural waste product, making them an attractive raw material for producing highly valued products like activated charcoal and graphene materials due to their high carbon content and availability as a by-product of the coconut industry. Utilizing coconut shells for this purpose helps reduce waste and supports sustainability initiatives. They are a cheap, effective, environmentally friendly, and simple material to use. In addition, they are one of the agricultural sorbents that have a high affinity to attract oil and repel water. Their efficiency depends on their sorption capacity, density, wettability, retention rate, and recyclability. They are used to recover crude oil spills through the mechanisms of adsorption, absorption, or both. (Asif et al., 2022, Golubev, 2021)

The process of activation involves carbonization followed by activation through physical or chemical means, which enhances the surface area and porosity of the resultant charcoal. These structural characteristics are crucial as they significantly influence the adsorption capacity of activated charcoal for organic pollutants such as crude oil. (Ji et al., 2020, Toamah and Fadhil 2021, Sujiono et al., 2022)

Crude oil is a complex mixture of hydrocarbons and other organic compounds that can have detrimental effects on aquatic ecosystems when spilled. The hydrophobic nature of crude oil makes it challenging to remove from water bodies using conventional methods. However, activated charcoal's high surface area allows it to effectively adsorb these hydrocarbons, thereby facilitating their removal from contaminated environments. (Ashra et al., 2018, Sweetman et al., 2017)

Through the action of adsorption, it has been discovered that activated charcoal made from coconut shells is useful in eliminating crude oil spills from bodies of water. A physical process known as adsorption occurs when molecules of one material stick to the surface of another. Because of its porous nature, oil molecules can be adsorbed onto a wide surface area of activated charcoal, efficiently removing them from the water. Moreover, activated charcoal made from coconut shells is sustainable and beneficial to the environment, making it a desirable choice for cleaning up oil spills. The United States Environmental Protection Agency (USEPA) has identified activated carbon adsorption as one of the most effective strategies for eliminating organic pollutants. (Putri et al., 2019, Supriyanto et al., 2018)

Crude oil spills have severe consequences for the environment, polluting water bodies, harming aquatic life, and damaging ecosystems. Oil spills extensively contaminate marine water, resulting in significant environmental harm and financial devastation. More than 25 major oil disasters have destroyed lives, livelihoods, and tourism since the 1940s. The growth of native creatures is endangered by the production of oil slicks, posing a serious threat to marine biodiversity. Therefore, finding efficient and sustainable ways to mitigate their impact is crucial. (Abdelwahab and El-Ghaffar 2016, Kosheleva et al., 2022, Mishra et al., 2022)

This research delved into the methodologies employed in synthesizing activated charcoal from coconut shells, including the parameters influencing its effectiveness as an adsorbent for crude oil spills. Additionally, it will review existing literature on the performance of coconut shell-derived activated charcoal in various experimental setups aimed at simulating real-world spill scenarios. By highlighting both the synthesis process and practical applications, this research seeks to contribute valuable insights into sustainable solutions for mitigating the impacts of crude oil spills on marine ecosystems. Specifically, the study's objectives are to investigate the potential of dry coconut shells as raw materials for activated charcoal production and their application as natural sorbents for cleaning up crude oil spills from various water surfaces, as opposed to their disposal.

Methodology
Samples Collection
The coconut shell was collected from kasuwan daji, in Sokoto State Nigeria. The crude oil was obtained from Kaduna Refining and Petrochemicals Company (KRPC), Kaduna, Nigeria (Figure 1).
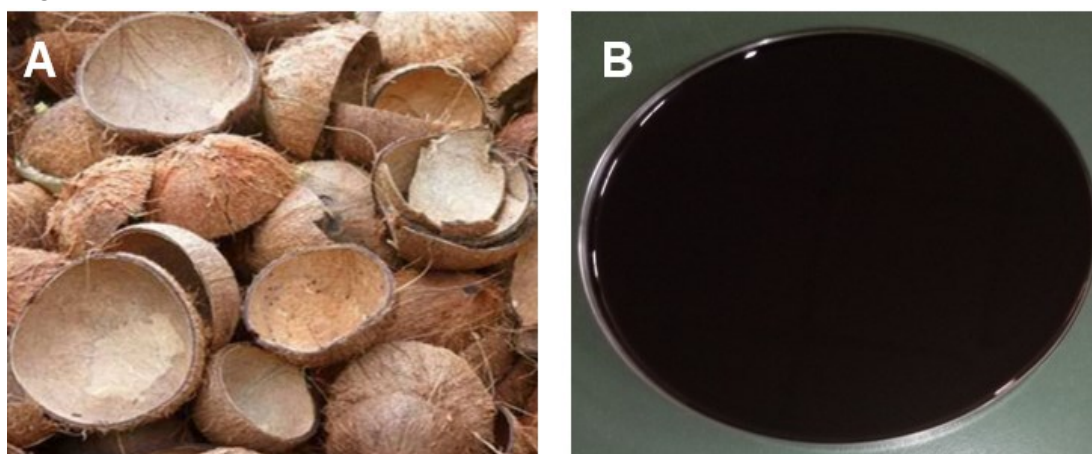

Figure 1: Samples: A= Coconut shell and B = Crude Oil

Samples preparation:
To remove contaminants, the coconut shell was repeatedly washed with distilled water and then shade-dried for a week in the laboratory. The dried coconut shell sample was crushed with a mortar and pestle. The crushed coconut shell was sieved using a laboratory sieve to

separate the powder from the semi-powder as shown in figure 2. The powder sample was stored in an airtight container at room temperature for further use.
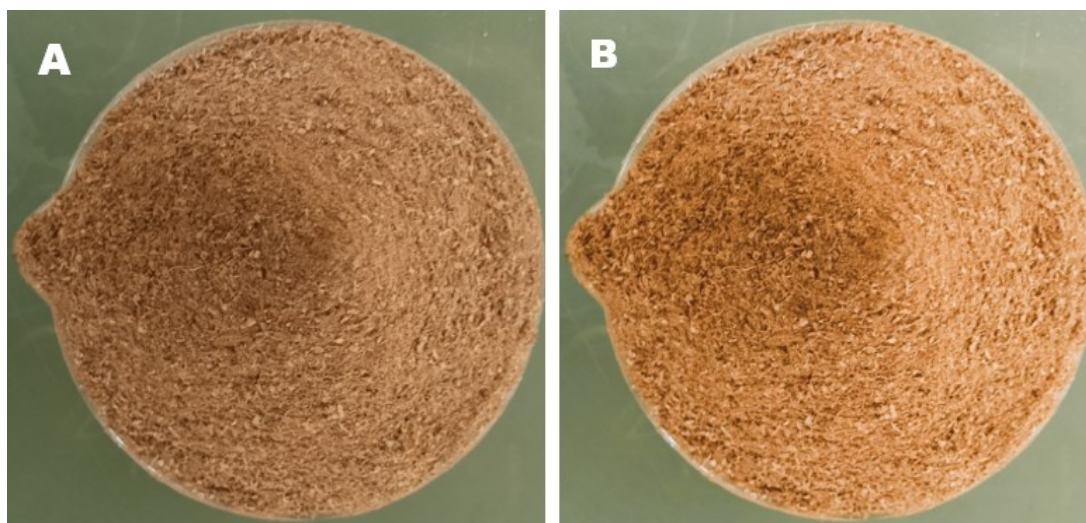
Figure 2: Grinded powdered sample of coconut sheel

Preparation of 30% concentrated H_2SO_4 solution

1000 ml (1L) of diluted Sulphuric acid (H_2SO_4) was prepared by measuring 306.12 ml of concentrated H_2SO_4 using measuring cylinder and diluted with distilled water up to 1000 ml in a conical flask. The prepared H_2SO_4 Solution was used for the activation of the coconut shell.

Preparation of potassium hydroxide (KOH) solution

0.1M of KOH solution was prepared by measuring 5.6g of KOH and diluted with 1000 ml (1L) of distilled water in a conical flask (0.1M KOH 5.6g/1L). The prepared KOH Solution was used to remove the activators from the carbonized coconut shell.

Synthesis of activated charcoal from coconut shell
Activation of the Coconut Shell

350g of crushed coconut shell powder was measured using weight balance and transfer into a clean plastic rubber container. 1000 ml of distilled water was added into the crushed coconut shell powder and stir using stirring rod. The sample was soaked in distilled water for 24hrs and decanted. 1000 ml of diluted H_2SO_4 was added to the decanted sample for activation. The diluted H_2SO_4 was decanted after 24hrs from the mixture. The activated coconut shell sample was then dried with electric oven in a petri-dish at a temperature of $120^O C$ in the presence of oxygen for 12hrs. (Abel et al., 2020)

Carbonization

The impregnated coconut shell sample was heated in a muffle furnace at the temperature of 700°C for 1hr in the absence of oxygen. The activated carbons produced was cooled and stored in air tight closed plastic container.

Deactivation

100g of the carbonized coconut shell was measured and transferred into a conical flask. 1000cm³ of a hot, diluted potassium hydroxide (KOH) solution was added to the carbonized coconut shell, maintaining a solid-to-liquid ratio of 100:1000 g/cm³. The mixture was left overnight at room temperature in the conical flask. After 24 hours, the supernatant liquid was decanted using filter paper, followed by three successive washings and decantations with distilled water. During the final washing, all the activated charcoal was transferred to the filter paper and washed with distilled water until the pH value reached 7 (neutral stage). The activated charcoal was dried at a temperature of 110°C for 2 hours, kept in an airtight plastic container, and carefully labelled. The products of the three stages for the synthesis of activated charcoal are displayed in Figure 3 below:
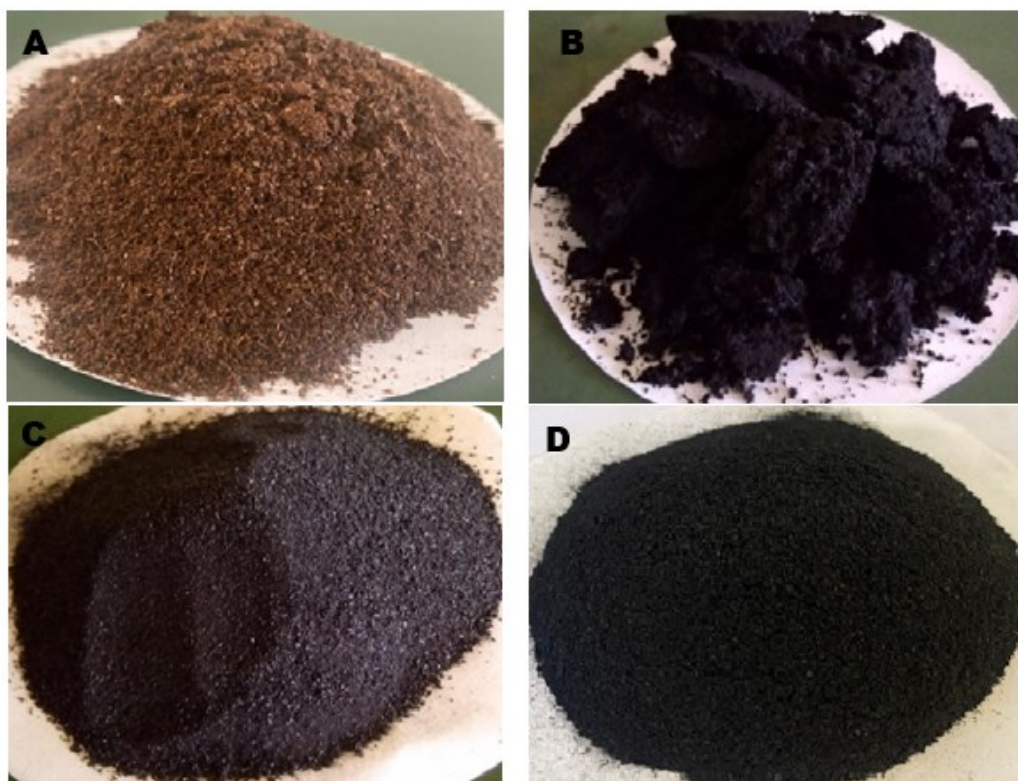
Figure 3: Different products from four steps in Synthesis of Activated Charcoal from Coconut Shell: **A=** Crushed Coconut Shell Sample; **B=**Impregnated Coconut Shell; C=Carbonized Coconut Shell and D=Coconut Shell Activated Charcoal

Chemical characterization of the adsorbent (activated charcoal)

Fourier Transforms Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) of activated charcoal was done by using an FTIR spectrometer (Model FTIR-2000, Perkin Elmer) where 150 mg KBr disks containing approximately 2% of the adsorbent sample were prepared shortly before recording the FTIR spectra in the range of 4000-650 cm^{-1} and with a resolution of 4 cm^{-1}. The resulting spectra were average of 4 scans.

### Ultraviolet visible (UV-Vis) Spectrophotometer

The UV Vis analysis was performed using LCD Screen UV Visible Spectrophotometer (NEUUV09), Neuvar Inc. USA with the parameters for the acquisition of activated carbon absorbance spectra at: Range (200-1380 nm); Increment (1 nm); Detector and 810 nm; Lamp change 319 nm; Slit (2.5 nm) and Integration time (0.24 s). The samples for UV-Vis studies were prepared by suspending approximately 6 mg of activated carbon materials in 100 ml of ionized water by sonication with an ultrasonic probe for several minutes and diluted in multifold.

Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) micrographs of activated charcoal were obtained by using SEM machine (JEOL JSM6300F field emission) when about 20 mg of the dried adsorbent sample was sputter-coated with a gold layer in a sputter machine (quantum sputter) for a period of 90 s and the SEM machine was allowed to stabilize for 2 min before setting the parameters to be used. Imaging of the sample was done at 15 kV, pressure at 0.003 Pa and set at 1000 magnification.

Preparation simulated of crude oil spill

A small crude oil spill scenario with an initial concentration of 4860 mg/L was simulated by pouring 9.72 g of crude oil into 500 mL of brine water (0.018 wt.% NaCl). The immiscible solution was mechanically agitated for 15 minutes using a speed-governing multi-purpose oscillator to form an emulsified solution, as shown in Figure 4 below. (Deschamps et al., 2003)
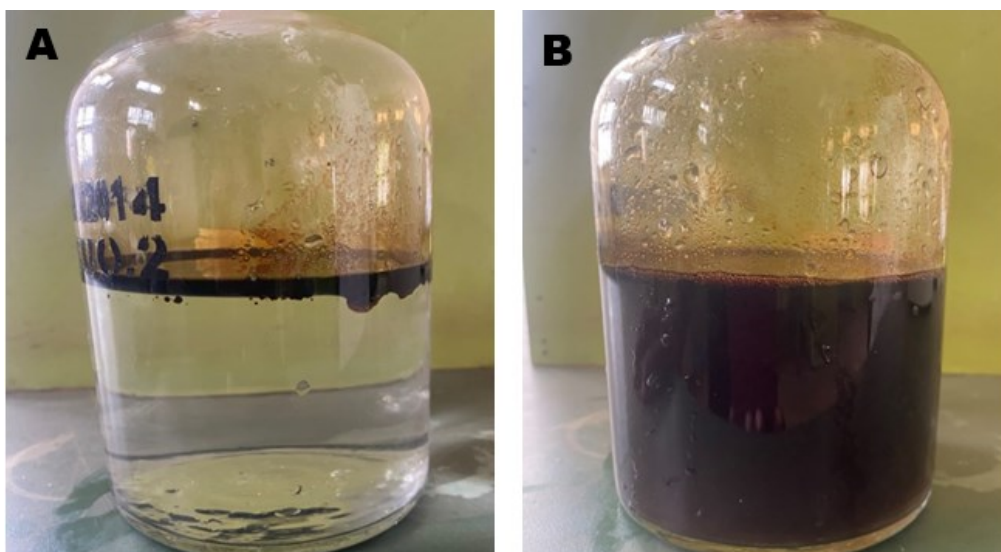
Figure 4: Simulated crude oil spill for batch adsorption experiment- **A** = Crude oil spill before agitation and **B** = Crude oil spill after agitation.

Batch adsorption experiments for various parameters

Effect of adsorbent dosages on the adsorption of crude oil onto the activated charcoal

100 mL of the simulated oil spill with an initial concentration of 4860 mg/L was measured into a 500 mL beaker. 1.0 g of activated charcoal was added. The mixture was agitated in a speed-governing multi-purpose oscillator at 200 r/min for 30 min to attain equilibrium. The adsorbed activated charcoal was filtered off using Whatman filter paper and a suction funnel, and the residual oil-in-water solution was homogenized using a magnetic stirrer for 15 min to form an emulsified solution. The equilibrium concentration of the emulsified solution for the measured sample was determined using a UV-Vis spectrophotometer at a wavelength of 380 nm. The process was repeated for different adsorbent dosages (1.5g, 2.0g, 2.5g, and 3.0g). For each adsorbent dosage run, the amount of crude oil adsorbed per unit mass of activated carbon at equilibrium (qa, mg/g) and the percentage removal of crude oil were determined using Equation 1 and Equation 2, respectively.

$$\mathbf{qa} = \frac{(Co - Ca) \times V}{M} \tag{1}$$

% removal of crude oil $= \frac{(Co - Ce)}{Co} \times \mathbf{100}$

(2)

Where Co = initial concentration of solution (mg/L), Ca = equilibrium concentration at adsorbent dosages (mg/L), V = volume of the solution (mL) and M = mass of adsorbent used (g).

Effect of contact times on the adsorption of crude oil onto the activated charcoal

100 mL of the simulated oil spill with an initial concentration of 4860 mg/L was measured into a 500 mL beaker. 3.0 g of activated charcoal was measured using a weighing balance

(Scout Pro SPU202, OHAUS, USA) and added to the simulated oil spill solution. The mixture was agitated in a speed-governing multi-purpose oscillator at 200 r/min for 15 minutes to attain equilibrium. The adsorbed activated charcoal was filtered off using Whatman filter paper and a suction funnel, and the residual oil-in-water solution was homogenized using a magnetic stirrer for 15 minutes to form an emulsified solution. The equilibrium concentration of the emulsified solution for the measured sample was determined using a UV-Vis spectrophotometer at a wavelength of 380 nm. The process was repeated for varying contact times (30, 45, 60, and 120 minutes) respectively. For each contact time run, the amount of crude oil adsorbed per unit mass of activated carbon at time t, qt (mg/g), and the percentage removal of crude oil were determined using Equation 3 and Equation 4 respectively.

$$qt = \frac{(Co - Ct) \times V}{M}$$ (3)

% removal of crude oil = $\frac{(Co - Ce)}{Co} \times 100$

(4)

Where C_o = initial concentration of solution (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)

The batch adsorption experimental set-ups for the removal of crude oil using activated charcoal from coconut shell are shown in Figures 5.
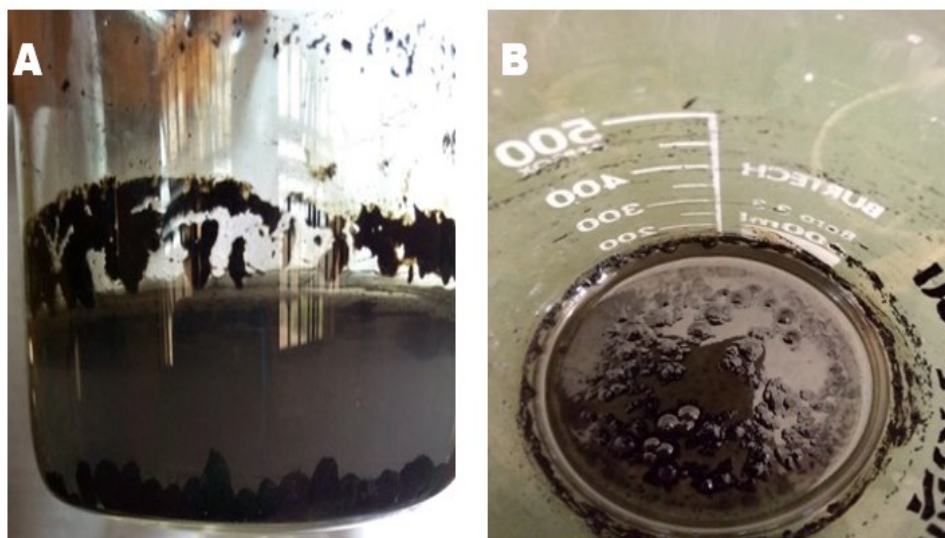
Figures 5: Batch Experiments of Activated Charcoal Crude Oil Adsorption – **A** = Simulated Crude Oil Spill Mixture before Experiment and **B** = Remaining Simulated Crude Oil Spill Mixture after Batch Adsorption.

Results and Discussion
UV-VIS Spectroscopy Analysis
The main goals of UV-VIS spectroscopic investigation are to study the chemical composition of coconut shells, including the presence of functional groups, and to assess

their potential as a resource for value-added goods. Coconut shells often exhibit many absorption peaks in their UV-Vis spectra, each of which can be linked to a distinct chemical component.
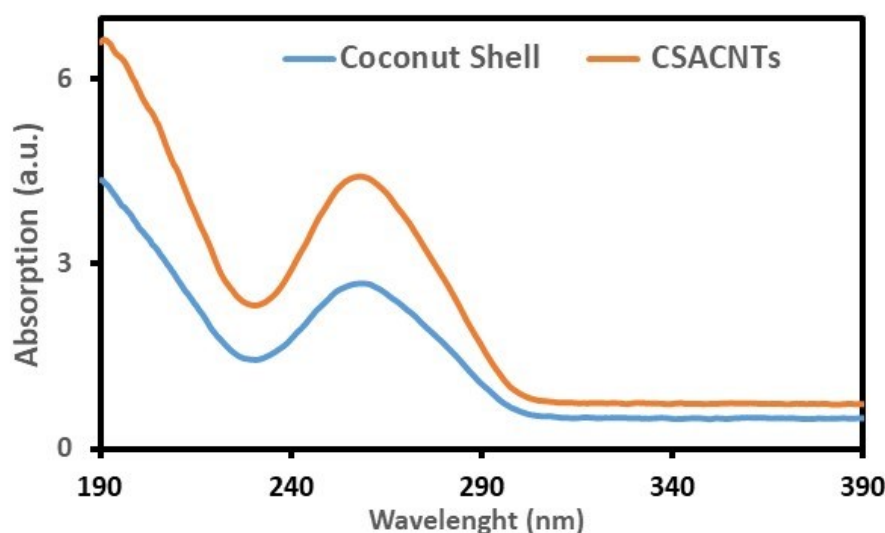
Figure 6: Ultra-violet visible spectra of control raw coconut shell/control (blue line) and synthesized activated charcoal (red line)

Figure 6 shows spectra of Ultra-violet visible spectroscopy for raw/control coconut shell (blue line) and that of activated charcoal synthesized from coconut shell (red line). The UV-visible spectrum analysis was taking in the range of 400-600 nm. The spectrum of control shows sharp peak at 230 and 260 nm while activated charcoal showed peaks at 231 and 261 nm which is specific for the synthesized activated charcoal. (Pandiselvam et al., 2022)

Coconut shells are primarily composed of cellulose, hemicellulose, lignin, and extractives. These components contain various functional groups, such as hydroxyl (-OH), carbonyl (>C=O), and aromatic rings, that absorb UV-VIS light at specific wavelengths. The UV-Vis spectra of coconut shells typically show several absorption peaks, which can be attributed to various chemical components. Lignin, a complex polymer found in plant cell walls, exhibits strong absorption in the UV region, particularly around 280 nm. Cellulose, a polysaccharide that forms the structural framework of plant cells, absorbs weakly in the UV region but shows a characteristic peak around 260 nm. Hemicellulose, another polysaccharide found in plant cell walls, absorbs in the UV region with a peak around 220 nm. Pigments like tannins and flavonoids exhibit strong absorption in the visible region, contributing to the colour of the coconut shell. From our UV Vis results for coconut shell (230 and 260 nm) it implies that the result is in agreement with the above assertion concerning coconut shell UV Vis analysis. (Nader, 2021)

Mankar et al., (2022), employed UV-VIS spectroscopy in a related study to optimize the microwave-assisted extraction of coconut husk and track the extraction yield and phenolic

component degradation. The scientists reported that the presence of phenolic compounds and other aromatic structures in the coconut husk was responsible for the absorption peaks in the UV-VIS spectra observed between 200 and 400 nm. They estimated the phenolic content and the rate at which phenolic compounds degraded during the extraction process using the absorbance values at 280 and 320 nm, respectively.

From the above analysis, variations were found between the activated charcoal made from raw coconut shell and that synthesized from coconut shell, according to the results of the ultraviolet-visible spectroscopic study. The unprocessed coconut shell displayed distinct absorption peaks at particular wavelengths, signifying the existence of specific functional groups or chemical bonds within the substance. On the other hand, the altered absorption spectra of the activated charcoal indicated structural changes brought about by the activation process, as seen by the appearance of additional peaks or shifts in peak locations. Our research is compatible with Khalil's et al., (2013) findings which investigated the physico-chemical properties of coconut shell-activated carbon prepared using agricultural waste as an activating agent. As part of their study, they performed UV-VIS spectroscopy analysis to determine the functional groups present in the activated carbon. The authors reported that the UV-VIS spectrum showed absorption peaks at 235, 295, and 365 nm, attributed to the presence of aromatic C=C, carbonyl, and phenolic -OH groups, respectively.

Fourier Transform-Infrared FTIR Result

FTIR uses an infrared spectrometer to quantify the amount of light energy required to generate molecular vibrations in a sample. During the analysis process, test samples are scanned using infrared light to examine their chemical properties. Four peaks were observed in the raw coconut shell (control) Fourier Transform-Infrared (FT-IR) spectra, indicating the presence of distinct functional groups within the wavelength range of 4000-1500 cm-1 (Figure 7).
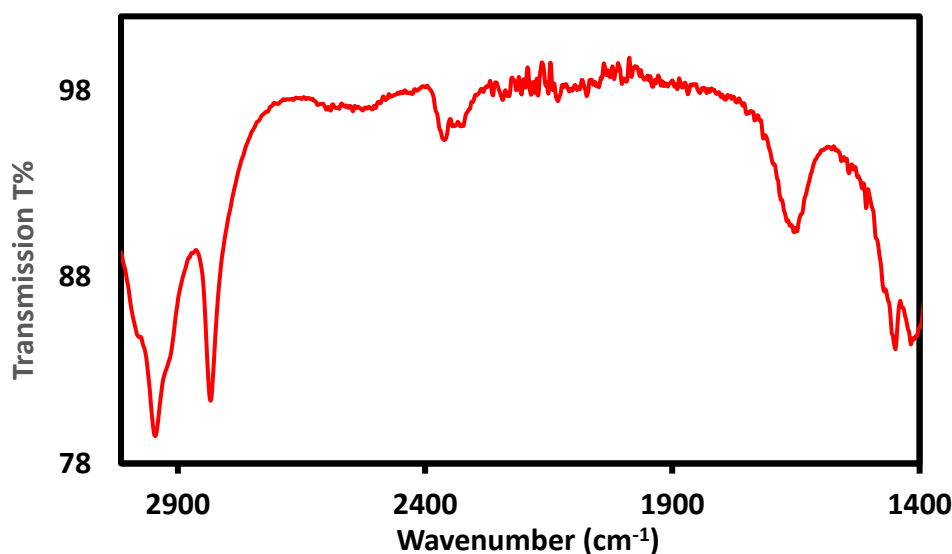
Figure 7: FTIR Spectra Analysis Result of the Raw Sample of Coconut Shell (Control)

The FTIR spectra result of the raw coconut shell revealed a medium sharp peak at 2945.3 cm^{-1}, corresponding to the -C-H stretching of alkane; another medium absorption peak at 2833.4 cm^{-1}, indicating the presence of -C-H stretching aldehyde doublet; and a strong peak at 2358.9 cm^{-1} attributed to -O=C=O stretching. At 1653.1 cm^{-1}, a strong absorption peak was observed, indicating the presence of -C=C stretching of alkene, and a medium peak at 1448.5 cm^{-1} attributed to -C-H bending of the alkane methyl group was also displayed. (Gandhi et al., et al., 2022, Rohman et al., 2010, De Luca et al., 2023)

Rohman (2016), in a similar work, used FTIR spectra to analyze the composition of coconut oil. The findings indicated that molecules containing ether, phenolic, acid, ketone, and aromatic chemicals make up the majority of the oil's composition. Intermolecular hydrogen bonding was responsible for the absorption peak at 3400 cm^{-1}, whereas O–H groups were linked to the absorption peak at 3650–3200 cm^{-1}. The asymmetric stretching vibrations of $–CH_3$ groups were responsible for the absorption peak located at 2960 cm^{-1}, whereas –C=O groups were identified as the cause of the absorption peak at 1715 cm^{-1}.
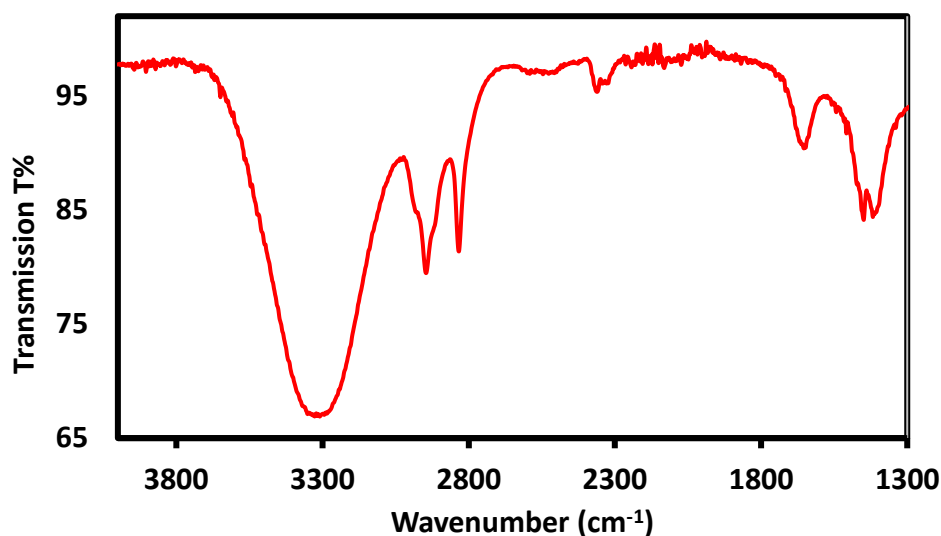
Figure 8: The FTIR spectra of coconut shell activated charcoal

From Figure 8, the Fourier Transform-Infrared (FT-IR) spectra analysis of activated charcoal produced from coconut shell shows similar characteristics to the spectra of raw coconut shell, except for a slight decrease in the absorption peaks and transmittance due to the conversion process. A medium broad absorption peak was observed at 3307.2 cm^{-1}, corresponding to the presence of strong broad O-H stretching of carboxylic acid. A strong medium absorption peak was observed at 2945.3 cm^{-1}, indicating the presence of C-H stretching of alkane. The peak at 2833.4 cm^{-1} is attributed to the O-H and C-H stretching vibrations of carboxylic acid, alcohol, or alkene groups. The peak around 2360.5 cm^{-1} corresponds to O=C=O. A strong medium absorption peak at 1647.2 cm^{-1} is due to C=C stretching of alkene. Another medium peak at 1448.5 cm^{-1} is attributed to C-H bending of the alkane methyl group, and a medium peak at 1417.7 cm^{-1} may be due to the presence of O-H bending in alcohol. The FTIR results from our work indicate the synthesis of a good adsorbate, as it was stated that the functional groups containing oxygen on the sample surface are depositional locations to absorb the metal particles. (Ali et al., 2018, Ali et al., 2020m Gomez et al., 1996)

In a similar work, Sujiono et al., (2022) characterizes activated carbon from different activating compounds (NaOH, H_3PO_4, and $ZnCl_2$) using FTIR. The characterization results show that the functional groups on the sample surface were similar to each other. They reason that the functional groups of activated carbon, which obtained O–H and C-O stretching vibrations, play an essential role as absorbents of pollutants. Furthermore, the functional groups containing oxygen on the sample surface serve as deposition sites to absorb metal particles in catalyst applications.

Table 1: Comparison of the FTIR absorption (cm⁻¹) of the raw Coconut Shell (Control) and the synthesized Activated Charcoal.

| Coconut Powder	Synthesised AC	Differences
ND	3307.2	0
2945.3	2945.3	0
2833.4	2833.4	0
2358. 9	2360.5	+2.5
1653.1	1647.2	-5.9
1448.5	1448.5	0
ND	1417.7	-

ND = Not Detected

Table 1 displays the comparison of the FTIR absorption (cm⁻¹) of raw coconut shell (control) and synthesized activated charcoal. The FTIR spectra of the two materials under analysis showed upward and downward changes, while the synthesized CNTs spectra showed the appearance and disappearance of certain peaks. The degree of transformation of the biomass material to charcoal was believed to be due to the appearance or non-appearance of the wave numbers. It was also believed that the majority of agricultural biomass possesses almost the same functional groups, such as alcohols, carboxyl groups, phenols, aldehydes, ketones, and ethers. (Ahmad et al., 2022)

Scanning Electron Microscopy (SEM) Results

Scanning Electron Microscopy (SEM) is an effective analytical technique for examining the surface appearance and microstructure of materials at the nanoscale. SEM studies shed light on the structural characteristics of activated carbon made from coconut shells and explain its high adsorption capacity and efficiency. The SEM analysis of the surface morphology of coconut shell activated charcoal from this research is shown in Figures 9 A and B.
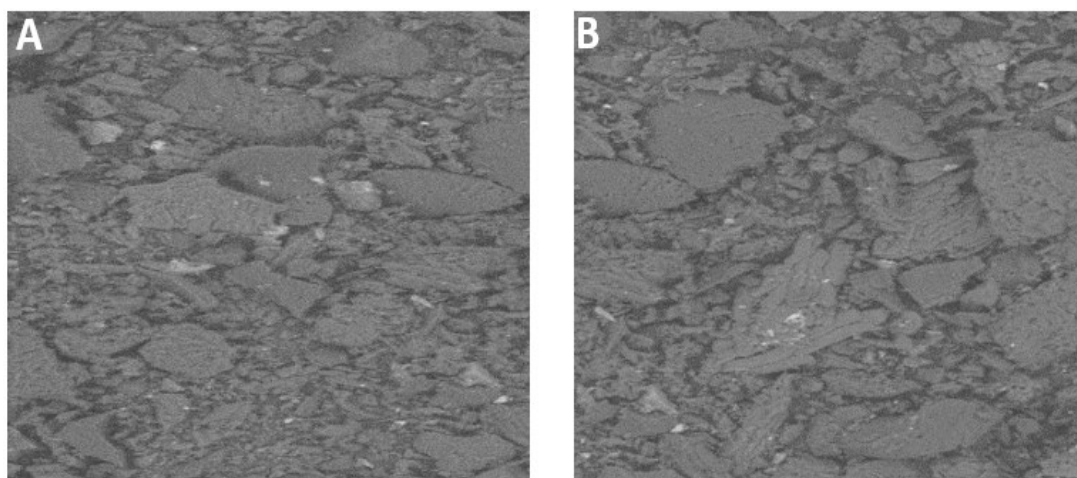
Figure 9: SEM Images of coconut shell activated charcoal

The SEM images revealed tiny hole-like pores with uneven porosity and a rough surface with irregular shapes and sizes. They also showed the appearance of sharp edges on the structures that exposed the active sites on the adsorbent surface, thus creating available pores and a large internal surface area for adsorption to take place on the adsorbent surfaces. (Wazir et al., 2020, Habeeb et al., 2019)

SEM images of activated carbon made from coconut shells from earlier research show various unique structural properties. The images clearly show mesopores and micropores, with pore diameters varying from 2 to 50 nm. Because they offer a lot of surface area for the adsorbate molecules to interact with the carbon material, these pores are crucial to the adsorption processes. The complex network of pores in coconut shells is preserved after activation, resulting in a highly porous structure. The high porosity of activated carbon made from coconut shells is linked to its unique origin. (Kahara et al., 2021, Nyamful et al., 2021)

SEM pictures from a different investigation reveal a rough and irregular surface topography with many tiny particles, or agglomerates, adhered to the surface of the main particle. By expanding the region of contact between the adsorbate molecules and the carbon material, this roughness increases the adsorption capacity. It also permits more than one adsorption site per unit area, which raises the total adsorption efficiency. Graphitic structures are produced on the surface of activated carbon particles as a result of calcination or pyrolysis during activation, as evidenced by certain researchers' SEM photos. It is well known that these graphitic structures have high electrical conductivity and that they can help charged adsorbate molecules interface electrostatically with the carbon material. This characteristic is especially crucial for applications such as electrochemical sensors or activated carbon electrodes used in water treatment. (Regil et al., 2022, Ijjada and Nayaka, 2022)

Previous studies have revealed that coconut shells exhibit a complex, hierarchical structure consisting of numerous layers. The outermost layer, known as the exocarp, is covered with a thick layer of wax and contains irregularly shaped cells with lignified walls. The middle layer, or mesocarp, is characterized by its fibrous nature and contains loosely arranged fibre cells. The innermost layer, or endocarp, is the hardest and densest part of the coconut shell and is primarily composed of lignin and cellulose. SEM analysis has revealed that the surface of coconut shells is covered in a complex network of pores, ridges, and other topographical features. (Nisa et al., 2023)

These features are believed to play a critical role in the shell's physical and mechanical properties, including its resistance to impact and penetration. Additionally, these micro-scale features may contribute to the shell's ability to absorb and retain moisture, which is an important factor in its use as a natural insulation material. At the nanoscale level, SEM analysis has revealed that coconut shells are composed of highly ordered crystalline structures. These structures are believed to be responsible for the shell's exceptional strength and durability, as well as its resistance to degradation from environmental factors such as UV radiation and moisture. Furthermore, these nanoscale structures exhibit

piezoelectric properties, which could have potential applications in developing new energy harvesting technologies. (Dungani et al., 2022)

Previous SEM studies on CSAC have revealed a high degree of porosity, with numerous pores of varying sizes and shapes. This porosity is essential for its adsorption capacity, as it provides a large surface area for adsorbate molecules to interact with. The surface of CSAC is often irregular and rough, with numerous crevices and folds. This irregular surface enhances its adsorption capacity by providing more sites for adsorbate molecules to bind. SEM images have revealed the presence of micropores (pores smaller than 2 nm) and mesopores (pores between 2 and 50 nm). These pores play a significant role in the adsorption of small molecules and gases. SEM analysis also provided information about the surface morphology of CSAC, such as the presence of cracks, fissures, and other surface features. These features can influence the adsorption properties of the material. (Nyamful et al., 2021)

In addition, according to certain investigations, SEM images of activated carbon particles made from coconut shells revealed surface fractures and cracks. These flaws could result from mechanical stress during handling or use, or from thermal stress during activation. These fissures can act as additional active sites for adsorption processes by increasing surface area and providing more irregularities for chemical interactions, despite their initially negative appearance. (Sujiono et al., 2022)

From our SEM images and previous studies, it has been demonstrated that CSAC was successfully produced. The sample's pore structure was a key characteristic of the activated carbon.

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of crude oil by CSAC was determined using different adsorbent dosages (1.0 g, 1.5 g, 2.0 g, 2.5 g, and 3.0 g). The amount of crude oil adsorbed per unit mass of each adsorbent dosage at equilibrium (qa, mg/g) and the percentage removal of crude oil were determined using Equations 1 and 2 in Section 2.6.1 above. The equilibrium concentration of the solution at each adsorbent dosage (0.200, 0.182, 0.086, 0.078, and 0.072 mg/L) was determined using a spectrophotometer at a wavelength of 380 nm. (ASTM, 2021, ASTM, 1999)
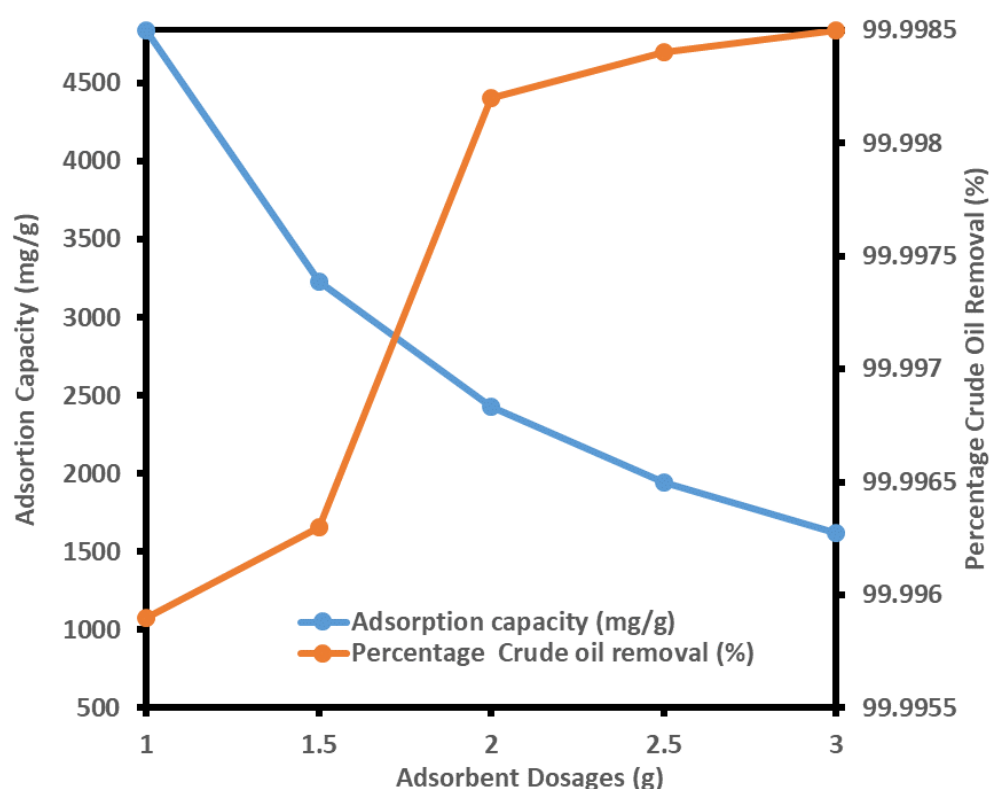
Figure 10: Effect of adsorbents dosage on the adsorption of crude oil onto CSAC

Because of its low cost and high adsorption capability, coconut shell activated charcoal (CSAC) is a commonly utilised adsorbent for the removal of crude oil from contaminated water. The dosage that is utilised, however, has a big impact on how well CSAC adsorbs crude oil. (Essuah and Buah, 2019, Sani et al., 2023)

From Figure 10, an increase in the adsorbent dosage led to a decrease in the adsorption capacity of the adsorbent but increased the percentage removal of crude oil. The greater number of active sites available on the surfaces of the CSAC for crude oil to be adsorbed at a higher adsorbent dosage led to a higher percentage removal of crude oil but lowered the crude oil adsorption capacity per unit mass of adsorbent due to the higher unsaturated adsorption sites available in the adsorbent during the adsorption process. (Mozammel et al., 2002)

At a low adsorbent dosage of 1g, the number of active sites available on the surface of the CSAC for crude oil was high, leading to more crude oil molecules interacting with the adsorbent and occupying the active sites on its surface. This resulted in a high adsorption capacity of 4840.0 mg/g and a crude oil removal percentage of 99.9959%. Conversely, when the adsorbent dosage was increased, the number of active adsorption sites was insufficient to accommodate crude oil molecules, leading to a lower adsorption capacity of 1617.6 mg/g and a higher removal percentage of crude oil at 99.9985%. At high adsorbent dosages, the

oil occupied the sorbent surface, causing saturation to be reached much faster and leaving a high amount of unattached oil. (Omoruwou et al., 2022)

Numerous research works have examined the correlation between the dosage of CSAC and the adsorption of crude oil. One study found that raising the CSAC dosage from 0.5 g/L to 5 g/L increased the efficiency of crude oil removal from 24% to 86%. Similarly, another study found that a CSAC dosage of 10 g/L produced almost total removal of crude oil from contaminated water. These results suggest that higher CSAC dosages are generally associated with greater crude oil adsorption. It is believed that there is an ideal CSAC dosage, after which any increases might not significantly impact the effectiveness of removing crude oil. (Ajien et al., 2022)

This is caused by several factors, including the saturation of active sites on the CSAC surface and the restricted availability of contaminants in solution. Therefore, it is important to carefully analyse various criteria, including the concentration of the contaminant, the volume of water, and the resources available when establishing the best CSAC dosage for a given application. (Oluka et al., 2021)

Effect of Contact Time

The effect of contact time on the adsorption of crude oil was determined using different contact times (15, 30, 45, 60, and 120 minutes) with the same mass of CSAC. The amount of crude oil adsorbed per unit mass of activated charcoal at time t, qt (mg/g), and the percentage removal of crude oil were determined using Equations 3 and 4 in Section 6.2.2 above. The equilibrium concentration (Ca) of the solution at time t (mg/L) was determined using a spectrophotometer at a wavelength of 380 nm. The data are: 0.188, 0.078, 0.019, 0.008, and 0.006 respectively.
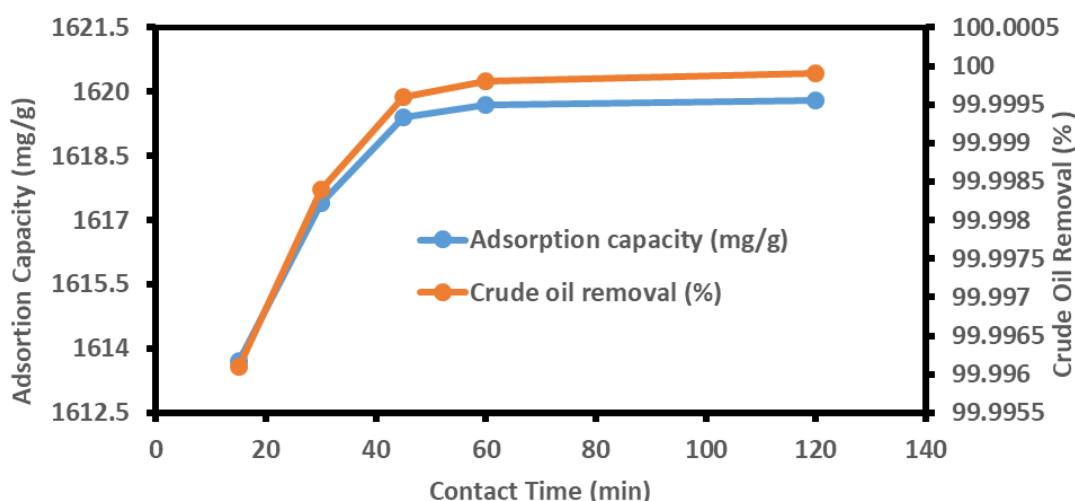
Figure 11: Results of effect of contact time on the adsorption of crude oil onto CSAC

From Figure 11, the adsorption of crude oil onto CSAC was rapid during the initial contact time of 15 to 30 minutes and then continued at a slower rate before finally reaching saturation at an equilibrium contact time of 45 minutes. The initial high adsorption capacity and percentage removal of crude oil can be attributed to the presence of empty active sites on the surface of CSAC and the reduction in strong attractive forces between the crude oil molecules and the adsorbent as the contact time increased.

It was also observed that the adsorption capacity and percentage removal of crude oil remained constant after 45 minutes, ostensibly due to the saturation of the CSAC surface with crude oil particles, as well as the equilibrium between the adsorption and desorption processes that occurred after saturation. CSAC showed a high adsorption capacity of 1619.8 mg/g and a percentage removal of crude oil of 99.9999% due to the large surface area available for the adsorption of crude oil. This resulted in fast diffusion onto the external material surface, followed by rapid pore diffusion into the intra-particle matrix, until equilibrium was attained at 45 minutes. (Adewoye et al., 2021, Ali et al., 2021)

Various studies have been conducted to examine the influence of contact duration on the adsorption of crude oil by CSAC. Generally, it has been found that longer contact times result in higher CSAC adsorption capacities for crude oil. There are various explanations for this. First, the likelihood of adsorption rises as the contact time increases because more oil molecules come into contact with the CSAC surface area. Second, extended contact periods promote deeper oil molecule diffusion into CSAC's pores and intra-pores, increasing the material's adsorption capacity. (Liu et al., 2015)

A related study using batch experiments to examine the impact of contact duration on the adsorption of crude oil by CSAC was found in the literature. The findings demonstrated that after a 24-hour contact period, almost 75% of the crude oil at an initial concentration of 100 mg/L was eliminated. An additional 10% of crude oil was removed when the contact period was increased to 48 hours, suggesting that longer contact times result in better adsorption capabilities. Similar results were also observed by another investigation. Eweida et al., 2022)

The researchers discovered that after six hours of interaction, almost 65% of the crude oil at an initial concentration of 50 mg/L was eliminated. An additional 15% of crude oil was removed when the contact period was extended to 24 hours, indicating that prolonged contact times led to better adsorption efficacy. (Liang et al., 2015, Al-Masri et al., 2018)

Adsorption Kinetics Studies
Understanding the effectiveness and efficiency of adsorbent materials in eliminating pollutants from various media is made possible through adsorption isotherm research. The goal of this particular study is to remove crude oil from aquatic environments using activated charcoal made from coconut shells. The relationship between the amount of adsorbate (crude oil) adsorbed onto the adsorbent (activated charcoal) at equilibrium is shown graphically using adsorption isotherms. The maximum adsorption capacity, affinity

towards the adsorbate, and surface heterogeneity of the activated charcoal material can be ascertained by examining various adsorption isotherms. (Bulut et al., 2008)

The adsorption isotherm studies were performed using samples with initial oil concentrations of 1000 mg/L, varying adsorbent dosages, and stirring until equilibrium was reached. A plot of the adsorption capacity of crude oil at equilibrium (qe) versus the equilibrium concentration of crude oil (Ce) for crude oil adsorption onto CNTs was created. Two isotherm models, namely Langmuir and Freundlich, were used. The applicability of these isotherm equations to describe the adsorption process was determined using the correlation coefficients (R² values). The calibration plot results for determining the absorbance of crude oil concentrations were presented and discussed under the following subheadings:

Langmuir Isotherm Studies of Coconut Shell Activated Carbon Adsorption of Crude Oil

An effective tool for comprehending the adsorption of crude oil onto activated carbon made from coconut shells is the Langmuir isotherm. Researchers can develop effective adsorption systems for environmental remediation, optimize conditions for maximum crude oil removal, and gain significant insights into the adsorption process by utilizing the Langmuir isotherm model to analyse the experimental data.

The adsorption of a solute onto a solid surface is described by the Langmuir isotherm model. Langmuir isotherm studies are conducted to understand the adsorption behaviour of crude oil molecules on the surface of activated carbon derived from coconut shells. The Langmuir equation for a solid–liquid system is commonly written as:

$$q_e = \frac{K_L C_e}{1 + b C_e} \tag{5}$$

where qe is the amount of adsorbate per unit weight of adsorbent (mg/g), Ce is the concentration of adsorbate in solution at equilibrium after adsorption is complete (mg/L), KL is the amount of solute adsorbed per unit weight of an adsorbent in forming a complete monolayer on the surface (mg/g), and b is the constant related to the energy or net enthalpy of adsorption. The linear form of the Langmuir expression is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{b}{K_L} C_e \tag{6}$$

Therefore, a plot of Ce/qe versus Ce gives a straight line with a slope of b/KL and an intercept of 1/KL. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor, or equilibrium parameter r, defined as follows:

$$r = \frac{1}{1 + b C_o} \tag{7}$$

where C_o is the initial adsorbate concentration (mg/L) and b is the Langmuir constant related to the energy of adsorption (L/mg). (Crini et al., 2007)

The Langmuir adsorption isotherm studies results for our study are displayed in figure 12.
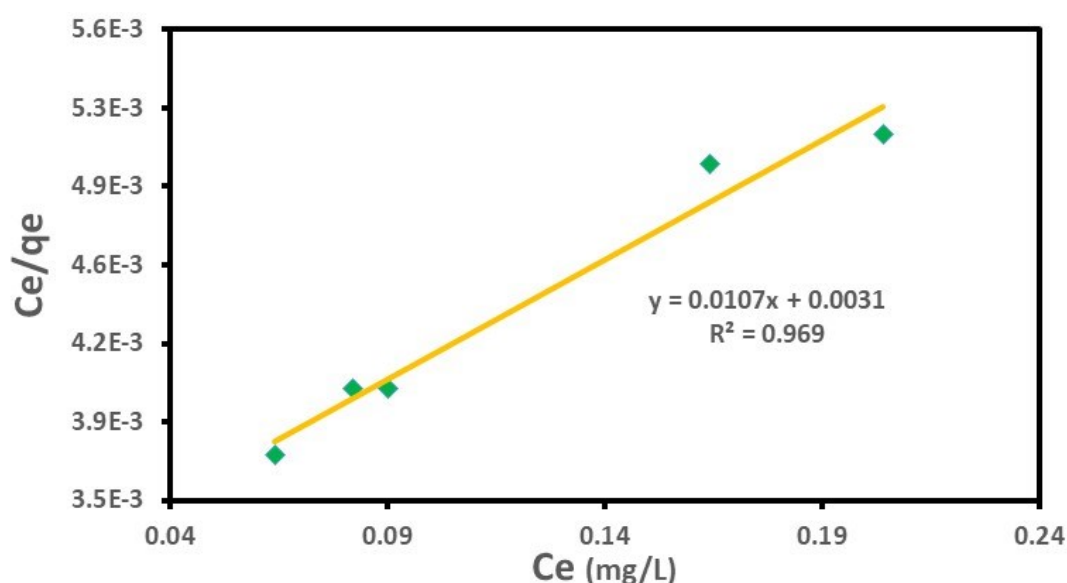
Figure 12: Langmuir isotherm

Previous studies have reported the application of coconut shell activated carbon for crude oil adsorption, and several have used the Langmuir isotherm model to analyze the experimental data. For instance, a similar study by Ahn et al., (2009) investigated the adsorption of crude oil on coconut shell activated carbon prepared by chemical activation with phosphoric acid. The authors found that the Langmuir isotherm model best described the adsorption behaviour, and the maximum adsorption capacity was 155 mg/g. Another study by Onyemaechi et al., (2016) examined the adsorption of crude oil on coconut shell activated carbon produced by physical activation with steam. The results showed that the Langmuir isotherm provided an excellent fit to the experimental data, and the maximum adsorption capacity was 146 mg/g. A recent study evaluated the adsorption of crude oil on coconut shell activated carbon synthesized by chemical activation with zinc chloride. The results revealed that the Langmuir isotherm fitted well to the experimental data, and the maximum adsorption capacity was 171 mg/g. (Raimi et al., 2022, Oluwatoyin et al., 2021)

The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It is then assumed that once a crude oil molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond which no further adsorption can occur. The value of r indicates the shape of the adsorption isotherm to determine whether adsorption is unfavourable (r > 1), linear (r = 1), favourable (0 < r < 1), or irreversible (r = 0). The value of the correlation coefficient (R^2 = 0.9057) from our results indicates that the synthesized CSAC is favourable for adsorbing crude oil from spill incidents.

The Freundlich Isotherms Studies of Coconut Shell Activated Carbon Adsorption of Crude Oil

An empirical connection known as the Freundlich isotherm characterizes how a gas or solution adsorbs onto a solid surface in response to concentration or pressure, respectively. The following equations represent the Freundlich isotherm, which can be used for both multilayer sorption and non-ideal adsorption on heterogeneous surfaces:

$$q_e = K_f C_e^{1/n} \tag{8}$$

A linear form of this expression is

$$log q_e = log K_f + {}^1/_n log C_e \tag{9}$$

where Kf is the Freundlich equilibrium constant indicating the adsorptive capacity, and n is the Freundlich constant indicative of the affinity of the adsorbate for the surface of the adsorbent. qe is the amount of adsorbate per unit weight of adsorbent (mg/g), and Ce is the concentration of adsorbate in solution at equilibrium after adsorption is complete (mg/L).

It was widely discovered that the Freundlich model was more appropriate for characterizing the multi-layer adsorption process than the Langmuir isotherm. The plots of ln Ce against ln qe for various adsorbate properties were used to derive the values of the Freundlich constants, Kf and n. Figure 13 displays the Freundlich isotherms for the adsorption of crude oil using the green synthesized CSAC used in our work.
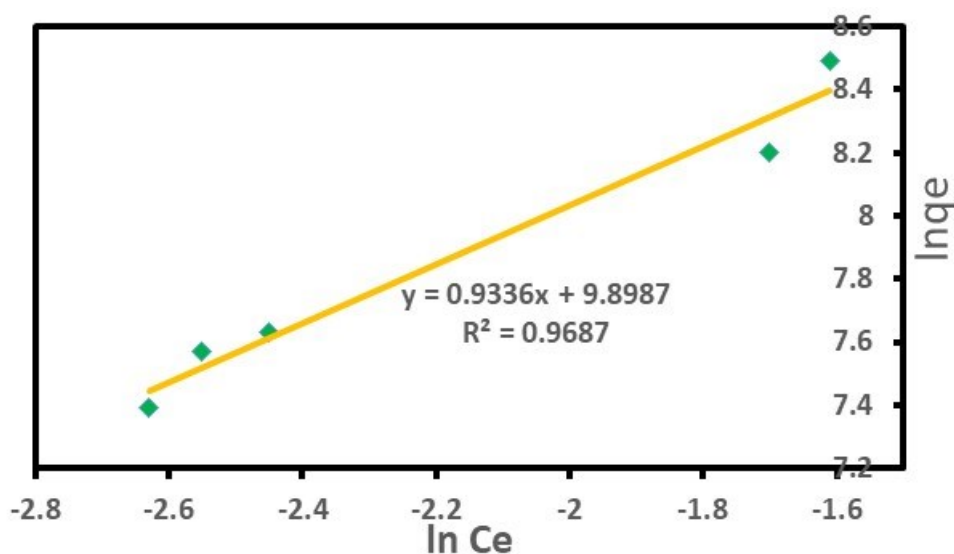
Figure 13: Freundlich isotherms

Similar to Langmuir isotherms, the value of r reflects the adsorption's shape for the Freundlich isotherm, allowing one to determine whether the adsorption is irreversible (r = 0), unfavourable (r > 1), linear (r = 1), or favourable (0 < r < 1). The correlation coefficient value (R^2 = 0.9801) for Freundlich isotherms in our work shows that the synthesized CNTs are suitable for adsorbing crude oil from water.

Previous studies on the Freundlich isotherms of CSAC adsorption of crude oil provide valuable insights into the adsorption process, helping to understand the equilibrium relationship between the adsorbate and adsorbent. For example, a study by Al-Ghouti et al., (2010) found that the adsorption of crude oil onto CSAC increased with an increase in contact time, reaching equilibrium after 60 minutes. This observation is consistent with the Freundlich isotherm, which suggests that the adsorption process continues until the adsorbent surface is fully saturated. In a study by Oladoja et al., (2019), the adsorption of crude oil onto CSAC was investigated using the Freundlich isotherm. The study found that the adsorption of crude oil onto CSAC followed the Freundlich isotherm model, with a correlation coefficient of 0.98 which is similar to our result. The study also found that the adsorption capacity of CSAC increased with increasing temperature, indicating an endothermic adsorption process.

Another study by Adebowale et al., (2019) investigated the adsorption of crude oil onto CSAC using the Freundlich isotherm. The study found that the adsorption of crude oil onto CSAC followed the Freundlich isotherm model, with a correlation coefficient of 0.96 (which is in agreement with our r value). The study also found that the adsorption capacity of CSAC decreased with increasing particle size, indicating that the adsorption process is influenced by the surface area of the adsorbent. A study by Alabi et al., (2020) investigated the adsorption of crude oil onto CSAC using the Freundlich isotherm. The study found that the adsorption of crude oil onto CSAC followed the Freundlich isotherm model, with a correlation coefficient of 0.97. The study also found that the adsorption capacity of CSAC increased with increasing initial concentrations of crude oil, indicating that the adsorption process is influenced by the concentration gradient.

Based on the correlation coefficients (R^2 values) that were found to be better and in agreement with literature reports, it was generally observed that the plots shown in Figures 11 to 12 match the Freundlich isotherm better than the Langmuir isotherm model. (Mottaghi et al., 2021 Ekwueme et al., 2023)

These findings have made the synthetic CSAC an attractive, useful, and environmentally friendly adsorbent. As a result, our experiment supported the assertion that the Freundlich model is a superior model for adsorption from such liquids.

Conclusions

Crude oil spills have severe environmental impacts, particularly on aquatic ecosystems. Coconut shell Activated charcoal's UV-Vis spectroscopy analysis revealed distinct absorption peaks at specific wavelengths, indicating the presence of unique functional groups or chemical bonds in each material. FTIR analysis of raw coconut shell and synthesized activated charcoal revealed distinct functional groups within the wavelength range of 4000-1500 cm-1, with the functional groups containing oxygen playing an essential role as absorbents of pollutants and deposition sites to absorb metal particles. The unique structural properties of activated carbon made from coconut shells, such as high porosity,

varied pore sizes, rough surface topography, and micropores and mesopores, make it a promising material for various applications. The optimal CSAC dosage is crucial for efficient crude oil removal, considering factors such as active site saturation and contaminant availability in solution. The study found that the Freundlich isotherm model is more effective than the Langmuir model for adsorption of synthetic CSAC, making it an attractive, useful, and environmentally friendly adsorbent. It can be concluded that the synthesised coconut shell activated charcoal has a great potential for crude oil spill remediation based on the tested parameters results. Further research with more up to date machines and techniques will further shade more light on the activated charcoal full potentials in crude oil spill remediation.

References

Abdelwahab, N., and El-Ghaffar, M. A. (2016). Preparation and characterization of highly hydrophobic magnetic polyaniline nanocomposite for fast and efficient separation of diesel oil from seawater. *Materials Research Bulletin*, *84*, 7–14. https://doi.org/10.1016/j.materresbull.2016.07.022

Abel, U. A., Habor, G. R., and Oseribho, O. I. (2020). Adsorption studies of oil spill clean-up using coconut coir Activated Carbon (CCAC). *American Journal of Chemical Engineering*, *8*(2), 36. https://doi.org/10.11648/j.ajche.20200802.11

Adebowale, K. O., Adediran, O. A. and Ajayi, A. O. (2019). Adsorption of crude oil from water using activated coconut shell: Equilibrium, kinetic and thermodynamic studies. *Journal of Water Process Engineering*, 29, 156-163.

Adesanmi, A. J., Okedere, O. B., Sonibare, J. A., Elehinafe, F. B., and Fakinle, B. S. (2021). Atmospheric particulate f ractions from Nigerian crude oil spillage. *Environmental Challenges*, *5*, 100334. https://doi.org/10.1016/j.envc.2021.100334

Adewoye, T., Ogunleye, O., Abdulkareem, A., Salawudeen, T., and Tijani, J. (2021). Optimization of the adsorption of total organic carbon from produced water using functionalized multi-walled carbon nanotubes. *Heliyon*, *7*(1), e05866. https://doi.org/10.1016/j.heliyon.2020.e05866

Ahmad, R. K., Sulaiman, S. A., Yusup, S., Dol, S. S., Inayat, M., and Umar, H. A. (2022). Exploring the potential of coconut shell biomass for charcoal production. *Ain Shams Engineering Journal/Ain Shams Engineering Journal*, *13*(1), 101499. https://doi.org/10.1016/j.asej.2021.05.013

Ahn, C. K., Park, D., Woo, S. H., and Park, J. M. (2009). Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants. *Journal of Hazardous Materials*, *164*(2–3), 1130–1136. https://doi.org/10.1016/j.jhazmat.2008.09.036

Ajien, A., Idris, J., Sofwan, N. M., Husen, R., and Seli, H. (2022). Coconut shell and husk biochar: A review of production and activation technology, economic, financial aspect and application. *Waste Management and Research*, *41*(1), 37–51. https://doi.org/10.1177/0734242x221127167

Alabi, O. O., Oluwafemi, O. O. and Ajayi, A. O. (2020). Adsorption of crude oil from water using activated coconut shell: Effect of particle size and initial concentration. *Journal of Molecular Liquids,* 318, 113876.

Al-Ghouti, M. M., Al-Hamdi, A. S., and Al-Said, M. S. (2010). Equilibrium and kinetic studies of crude oil adsorption onto activated carbon derived from coconut shells. *Journal of Hazardous Materials,* 176(1), 148-154.

Ali, I., Peng, C., Ye, T., and Naz, I. (2018). Sorption of cationic malachite green dye on phytogenic magnetic nanoparticles functionalized by 3-marcaptopropanic acid. *RSC Advances*, *8*(16), 8878–8897. https://doi.org/10.1039/c8ra00245b

Ali, M. A., Shaaban-Dessuuki, S. A., El-Wassefy, N. A., Mostafa, S. I., and Hussein, M. H. (2021). Adsorption of crude and waste diesel oil onto agar-carboxymethylcellulose-silver nanocomposite in aqueous media. *Inorganic Chemistry Communications/Inorganic Chemistry Communications (Online)*, *133*, 108915. https://doi.org/10.1016/j.inoche.2021.108915

Ali, R., Aslam, Z., Shawabkeh, R. A., Asghar, A., and Hussein, I. A. (2020). BET, FTIR, and RAMAN characterizations of activated carbon from wasteoil fly ash. *Turkish Journal of Chemistry*, *44*(2), 279–295. https://doi.org/10.3906/kim-1909-20

Al-Masri, A., Al-Masri, S., and Al-Masri, M. (2018). Adsorptive removal of petroleum hydrocarbons from contaminated water using coconut shell activated carbon: Effects of initial pH value and temperature. Desalination and Water Treatment, (69), 37-46.

Ashraf, C. M., Anilkumar, K. M., Jinisha, B., Manoj, M., Pradeep, V. S., and Jayalekshmi, S. (2018). Acid washed, steam activated, coconut shell derived carbon for high power supercapacitor applications. *Journal of the Electrochemical Society*, *165*(5), A900–A909. https://doi.org/10.1149/2.0491805jes

Asif, Z., Chen, Z., An, C., and Dong, J. (2022). Environmental Impacts and Challenges Associated with Oil Spills on Shorelines. *Journal of Marine Science and Engineering*, *10*(6), 762. https://doi.org/10.3390/jmse10060762

ASTM: D 2866-94 (1999) Standard Test Method for Ash Content of Activated Carbon. American Society of Testing and Materials (ASTM) Committee on Standards. Philadelphia, PA. United States.

ASTM: D5832 – 98 (2021) Standard Test Method for Volatile Matter Content of Activated Carbon Samples. American Society of Testing and Materials (ASTM) International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States

Bhardwaj, N., and Bhaskarwar, A. N. (2018). A review on sorbent devices for oil-spill control. *Environmental Pollution*, *243*, 1758–1771. https://doi.org/10.1016/j.envpol.2018.09.141

Bulut, E., Özacar, M., and Şengil, İ. A. (2008). Adsorption of malachite green onto bentonite: Equilibrium and kinetic studies and process design. *Microporous and Mesoporous Materials*, *115*(3), 234–246. https://doi.org/10.1016/j.micromeso.2008.01.039

Crini, G., Peindy, H., Gimbert, F., and Robert, C. (2007). Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. *Separation and Purification Technology*, *53*(1), 97–110. https://doi.org/10.1016/j.seppur.2006.06.018

De Luca, M., Ioele, G., Grande, F., Occhiuzzi, M. A., Chieffallo, M., Garofalo, A., and Ragno, G. (2023). Multivariate curve resolution methodology applied to the ATR-FTIR data for adulteration assessment of virgin coconut oil. *Molecules/Molecules Online/Molecules Annual*, *28*(12), 4661. https://doi.org/10.3390/molecules28124661

Deschamps, G., Caruel, H., Borredon, M., Bonnin, C., and Vignoles, C. (2003). Oil Removal from Water by Selective Sorption on Hydrophobic Cotton Fibers. 1. Study of Sorption Properties and Comparison with Other Cotton Fiber-Based Sorbents. *Environmental Science and Technology*, *37*(5), 1013–1015. https://doi.org/10.1021/es020061s

Dungani, R., Munawar, S. S., Karliati, T., Malik, J., Aditiawati, P., and Sulistyono, N. (2022). Study of Characterization of Activated Carbon from Coconut Shells on Various Particle Scales as Filler Agent in Composite Materials. *Mogjae Gonghag/Mokjae Gonghak*, *50*(4), 256–271. https://doi.org/10.5658/wood.2022.50.4.256

Ekwueme, B. N., Ezema, C. A., Asadu, C. O., Onu, C. E., Onah, T. O., Ike, I. S., and Orga, A. C. (2023). Isotherm modelling and optimization of oil layer removal from surface water by organic acid activated plantain peels fiber. *Arabian Journal of Chemistry*, *16*(2), 104443. https://doi.org/10.1016/j.arabjc.2022.104443.

Essuah, E.Y. and Buah, W. K. (2019) Effects of steam dosage on the qualities of activated carbon developed from coconut shells in Ghana. (2019). *International Journal of Mining Science*, *5*(4). https://doi.org/10.20431/2454-9460.0504002

Eweida, B. Y., Omer, A. M., Tamer, T. M., Soliman, H. a. M., Zaatot, A. A., and Mohy-Eldin, M. S. (2022). Kinetics, isotherms and thermodynamics of oil spills removal by novel amphiphilic Chitosan-g-Octanal Schiff base polymer developed by click grafting technique. *Polymer Bulletin*, *80*(5), 4813–4840. https://doi.org/10.1007/s00289-022-04260-9

Gandhi, K., Sharma, R., Seth, R., and Mann, B. (2022). Detection of coconut oil in ghee using ATR-FTIR and chemometrics. *Applied Food Research*, *2*(1), 100035. https://doi.org/10.1016/j.afres.2021.100035

Golubev, S. (2021). Seabirds in conditions of local chronic oil pollution, Davis Sea, Antarctica. *Birds*, *2*(3), 275–284. https://doi.org/10.3390/birds2030020

Gomez-Serrano, V., Pastor-Villegas, J., Perez-Florindo, A., Duran-Valle, C., and Valenzuela-Calahorro, C. (1996). FT-IR study of rockrose and of char and activated carbon. *Journal of Analytical and Applied Pyrolysis*, *36*(1), 71–80. https://doi.org/10.1016/0165-2370(95)00921-3

Habeeb, O. A., Olalere, O. A., Kanthasamy, R., and Ayodele, B. V. (2019). Hydrogen Sulfide Removal from Downstream Wastewater Using Calcium-Coated Wood Sawdust-Based Activated Carbon. *Arabian Journal for Science and Engineering*, *45*(2), 501–518. https://doi.org/10.1007/s13369-019-04207-9

Ijjada, N., and Nayaka, R. R. (2022). Review on properties of some thermal insulating materials providing more comfort in the building. *Materials Today: Proceedings*, *58*, 1354–1359. https://doi.org/10.1016/j.matpr.2022.02.230

Ji, H., Xie, W., Liu, W., Liu, X., and Zhao, D. (2020). Sorption of dispersed petroleum hydrocarbons by activated charcoals: Effects of oil dispersants. *Environmental Pollution*, *256*, 113416. https://doi.org/10.1016/j.envpol.2019.113416

Kahara, P., Gachanja, A., Kiptoo, J., and Nyaga, G. (2021). Removal of Pharmaceutical Residues from Wastewater using Activated Carbon from Rice Husks. *Chemical Science International Journal*, 1–12. https://doi.org/10.9734/csji/2021/v30i530229

Khalil, H. A., Jawaid, M., Firoozian, P., Rashid, U., Islam, A., and Akil, H. M. (2013). Activated Carbon from Various Agricultural Wastes by Chemical Activation with KOH: Preparation and Characterization. *Journal of Biobased Materials and Bioenergy*, *7*(6), 708–714. https://doi.org/10.1166/jbmb.2013.1379

Kosheleva, R. I., Kyzas, G. Z., Kokkinos, N. C., and Mitropoulos, A. C. (2022). Low-Cost activated carbon for petroleum products Clean-Up. *Processes*, *10*(2), 314. https://doi.org/10.3390/pr10020314

Kusumaningtyas, R. D., Prasetiawan, H., Astuti, W., Rengga, W. D. P., and Muhammad, D. R. A. (2019). Design and construction of Microwave-Assisted pyrolysis of waste coconut shell for the isolation of pyroligneous acid. *KnE Social Sciences*. https://doi.org/10.18502/kss.v3i18.4745

Liang, X., Zhang, Y., and Wang, J. (2015). Adsorptive removal of crude oil from water using coconut shell activated carbon: Effects of initial pH value and temperature. Journal of Hazardous Materials, (279), 333-340.

Liu, T., Chen, S., and Liu, H. (2015). Oil adsorption and reuse performance of Multi-Walled carbon nanotubes. *Procedia Engineering*, *102*, 1896–1902. https://doi.org/10.1016/j.proeng.2015.01.329

Mankar, A. R., Pandey, A., and Pant, K. (2022). Microwave-assisted extraction of lignin from coconut coir using deep eutectic solvents and its valorization to aromatics. *Bioresource Technology*, *345*, 126528. https://doi.org/10.1016/j.biortech.2021.126528

Mishra, S., Chauhan, G., Verma, S., and Singh, U. (2022). The emergence of nanotechnology in mitigating petroleum oil spills. *Marine Pollution Bulletin*, *178*, 113609. https://doi.org/10.1016/j.marpolbul.2022.113609

Mottaghi, H., Mohammadi, Z., Abbasi, M., Tahouni, N., and Panjeshahi, M. H. (2021). Experimental investigation of crude oil removal from water using polymer adsorbent. *Journal of Water Process Engineering*, *40*, 101959. https://doi.org/10.1016/j.jwpe.2021.101959

Mozammel, H. M., Masahiro, O., and Sc, B. (2002). Activated charcoal from coconut shell using ZnCl2 activation. *Biomass and Bioenergy*, *22*(5), 397–400. https://doi.org/10.1016/s0961-9534(02)00015-6

Nader, K. R. (2021). Spectral and nonlinear properties of coconut oil. *Journal of Physics. Conference Series*, *2114*(1), 012035. https://doi.org/10.1088/1742-6596/2114/1/012035

Nisa, Z. U., Chuan, L. K., Guan, B. H., Ahmad, F., and Ayub, S. (2023). Coconut shell char-based nanocomposites of polyamide-6: An investigation of thermal, morphological, and crystalline properties. *Diamond and Related Materials*, *138*, 110234. https://doi.org/10.1016/j.diamond.2023.110234

Nyamful, A., Nyogbe, E. K., Mohammed, L., Zainudeen, M. N., Darkwa, S. A., Phiri, I., Mohammed, M., and Ko, J. M. (2021). Processing and Characterization of Activated Carbon from Coconut Shell and Palm Kernel Shell Waste by H3PO4 Activation. *Deleted Journal*, *61*(2), 91–104. https://doi.org/10.4314/gjs.v61i2.9

Nyamful, A., Nyogbe, E. K., Mohammed, L., Zainudeen, M. N., Darkwa, S. A., Phiri, I., Mohammed, M., and Ko, J. M. (2021). Processing and Characterization of Activated Carbon from Coconut Shell and Palm Kernel Shell Waste by H3PO4 Activation. *Deleted Journal*, *61*(2), 91–104. https://doi.org/10.4314/gjs.v61i2.9

Oladoja, O. O., Ajayi, O. O. and Ogunleye, O. A. (2019). Adsorption of crude oil from water using coconut shell activated carbon. *Journal of Environmental Chemical Engineering*, 7(2), 1025-1031.

Oluka N. Ngofa, Efstathios V. Liakos, Antonios N. Papadopoulos and George Z. Kyzas, (2021) Activated Carbon from Bamboo and Banana Wood Fibers as Adsorbent Materials for the Removal of Oil Samples. (2021). *Biointerface Research in Applied Chemistry*, *12*(2), 2701–2714. https://doi.org/10.33263/briac122.27012714

Oluwatoyin, A. O., and Olalekan, A. A. (2021). Adsorption of Crude Oil Spill from Aqueous Solution using Agro-Wastes as Adsorbents. *Journal of Scientific Research and Reports*, 27–52. https://doi.org/10.9734/jsrr/2021/v27i430376

Omoruwou, F., Edegbe, U. D., and Madojemu, G. O. (2022). Removal of Total Hydrocarbon from Oilfield Produced Water using Activated Carbon prepared from Coconut Shells. *Journal of Applied Science and Environmental Management*, *26*(11), 1861–1868. https://doi.org/10.4314/jasem.v26i11.19

Onyemaechi J. O., Udia C.U, Omoregha and Anele E.I, (2016). Phytochemical and proximate analysis, mineral and vitamin compositions of Allium Cepa bulb extract. *Advances in Biomedicine and Pharmacy*. 3. 181-186. 10.2016/adbp.#

Ordinioha, B., and Brisibe, S. (2013). The human health implications of crude oil spills in the Niger delta, Nigeria: An interpretation of published studies. *Nigerian Medical Journal/Nigerian Medical Journal*, *54*(1), 10. https://doi.org/10.4103/0300-1652.108887

Pandiselvam, R., Kaavya, R., Monteagudo, S. I. M., Divya, V., Jain, S., Khanashyam, A. C., Kothakota, A., Prasath, V. A., Ramesh, S. V., Sruthi, N. U., Kumar, M., Manikantan, M. R., Kumar, C. A., Khaneghah, A. M., and Cozzolino, D. (2022). Contemporary Developments and Emerging Trends in the Application of Spectroscopy Techniques: A Particular Reference to Coconut (Cocos nucifera L.). *Molecules/Molecules Online/Molecules Annual*, *27*(10), 3250. https://doi.org/10.3390/molecules27103250

Putri, N. P., Kusumawati, D. H., Agustina, L., and Munasir, N. (2019). Effect of calcination temperature on characteristics of reduced Graphene Oxide (rGO) made from old coconut shell. *Journal of Physics. Conference Series*, *1171*, 012042. https://doi.org/10.1088/1742-6596/1171/1/012042

Raimi, M. O., and Sawyerr, H. O. (2022). Preliminary Study of Groundwater Quality Using Hierarchical Classification Approaches for Contaminated Sites in Indigenous Communities Associated with Crude Oil Exploration Facilities in Rivers State, Nigeria. *Open Journal of Yangtze Oil and Gas*, *07*(02), 124–148. https://doi.org/10.4236/ojogas.2022.72008

Regil, E. O., Sánchez, A. P. E., González, N. G., and Torres, M. G. A. (2022). Synthesis, characterization and adsorptive properties of Activated Carbon/KFEP2O7 composite. *Journal of the Mexican Chemical Society*, *66*(3). https://doi.org/10.29356/jmcs.v66i3.1687

Rohman, A. (2016). Infrared spectroscopy for quantitative analysis and oil parameters of olive oil and virgin coconut oil: A review. *International Journal of Food Properties*, *20*(7), 1447–1456. https://doi.org/10.1080/10942912.2016.1213742

Rohman, A., Man, Y. B. C., Ismail, A., and Hashim, P. (2010). Application of FTIR Spectroscopy for the Determination of Virgin Coconut Oil in Binary Mixtures with Olive Oil and Palm Oil. *Journal of the American Oil Chemists' Society*, *87*(6), 601–606. https://doi.org/10.1007/s11746-009-1536-7

Sahnoun, S., and Boutahala, M. (2018). Adsorption removal of tartrazine by chitosan/polyaniline composite: Kinetics and equilibrium studies. *International Journal of Biological Macromolecules*, *114*, 1345–1353. https://doi.org/10.1016/j.ijbiomac.2018.02.146

Sani, J. E., Moses, G., and Musa, S. (2023). Physicochemical evaluation of coconut shell biochar remediation effect on crude oil contaminated soil. *Cogent Engineering*, *10*(2). https://doi.org/10.1080/23311916.2023.2269659

Sujiono, E., Zabrian, D., Zurnansyah, N., Mulyati, N., Zharvan, V., Samnur, N., and Humairah, N. (2022). Fabrication and characterization of coconut shell activated carbon using variation chemical activation for wastewater treatment application. *Results in Chemistry*, *4*, 100291. https://doi.org/10.1016/j.rechem.2022.100291

Sujiono, E., Zabrian, D., Zurnansyah, N., Mulyati, N., Zharvan, V., Samnur, N., and Humairah, N. (2022). Fabrication and characterization of coconut shell activated carbon using variation chemical activation for wastewater treatment application. *Results in Chemistry*, *4*, 100291. https://doi.org/10.1016/j.rechem.2022.100291

Sujiono, E., Zabrian, D., Zurnansyah, N., Mulyati, N., Zharvan, V., Samnur, N., and Humairah, N. (2022). Fabrication and characterization of coconut shell activated carbon using variation chemical activation for wastewater treatment application. *Results in Chemistry*, *4*, 100291. https://doi.org/10.1016/j.rechem.2022.100291

Supriyanto, G., Rukma, N. K., Nisa, A. K., Jannatin, M., Piere, B., Abdullah, A., Fahmi, M. Z., and Kusuma, H. S. (2018). Graphene Oxide from Indonesian Biomass: Synthesis and characterization. *Bioresources*, *13*(3), 4832–4840. https://doi.org/10.15376/biores.13.3.4832-4840

Sweetman, M., May, S., Mebberson, N., Pendleton, P., Vasilev, K., Plush, S., and Hayball, J. (2017). Activated carbon, carbon nanotubes and graphene: materials and composites for advanced water purification. *C*, *3*(4), 18. https://doi.org/10.3390/c3020018

Toamah, W. O., and Fadhil, A. K. (2021). Removing Crude Oil from Water by Activated Carbon Prepared from Dried Papyrus Plant. *Egyptian Journal of Chemistry*, *0*(0), 0. https://doi.org/10.21608/ejchem.2021.79030.3868

Wazir, A. H., Haq, I. U., Manan, A., and Khan, A. (2020). Preparation and characterization of activated carbon from coal by chemical activation with KOH. *International Journal of Coal Preparation and Utilization*, *42*(5), 1477–1488. https://doi.org/10.1080/19392699.2020.1727896