



Corrective Removal of Pollutant from Contaminated Crude Oil Using Green Synthesized Activated Carbon Nanotubes

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ABSTRACT

The expanding global economy led to a continuous rise in transportation and the use of crude oil. The crude oil spill has been deemed a significant threat to both aquatic and terrestrial ecosystems. This paper aims to synthesize Carbon nanotubes (CNTs) and evaluate their potentials for removing crude oil spills. The research focuses on two parameters: adsorbent dosage and contact time. It investigated the adsorption of crude oil utilizing synthesized carbon nanotubes (CNT) derived from coconut shell. The investigation was conducted using batch adsorption, with the adsorbent dosage and contact time being varied as factors. The carbon nanotubes (CNT) that were synthesized were examined using Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet-Visible Spectroscopy (Uv-Vis), and Scanning Electron Microscopy (SEM) methods. The results revealed that the produced carbon nanotubes (CNTs) were within the nanoscale and have a high ratio of surface area to mass, indicating exceptional crystallinity. The morphological alteration greatly enhanced the hydrophobic nature of the adsorbent, resulting in the synthesis of a carbon nanotube (CNT) with dramatically improved crude oil adsorption capacity, reaching a maximum of 4855.8 mg/g. The experimental findings revealed a direct relationship between the quantity of adsorbent used and the percentage of crude oil that was eliminated. Likewise, a greater duration of contact resulted in a higher percentage of crude oil being removed. Carbon nanotubes synthesized, offer an excellent structure for effectively purifying contaminated crude oil. **Key words:** Carbon nanotubes (CNT), Carbon-based nanoparticles, Environmental remediation, Green synthesis.

1.0 INTRODUCTION

There has been an increasing worldwide interest in Nanoscience in recent years (Sadegh *et al.*, 2016). Investigation into nanoparticles is necessary in the present era, encompassing both application and production. The emergence and advancement of nanomaterials have presented the world with a fresh possibility and wider outlook on what can be accomplished by manipulating materials at the nanoscale. This has resulted in a global shift in the way we live, as nanomaterials find applications in diverse industries (Sabzehmeidani *et al.*, 2021). Nanoparticles (NPs) possess a distinct attribute of exhibiting a significantly higher surface to volume ratio in comparison to their larger counterparts. This makes them more suitable for specific applications among the many available nanoparticles (Baby *et al.*, 2019). Nanoscale structures, or nanostructures, are situated at the interface between the tiniest human-engineered devices and the biggest molecules found in biological organisms. The capacity to govern and manage these nanostructures will enable us to investigate novel physical, biological, and chemical characteristics of systems that lie between individual atoms, molecules, and bulk materials (Allan *et al.*, 2012).

Nanotechnology is extensively utilised in diverse fields, including environmental research, health sciences,

electronics, industrial separation, catalysts, energy storage, and energy generation (Zeng, 2018). Nanomaterials provide an exceptional framework for the purification of contaminated oil due to their extensive surface area, ability to endure chemical alterations, and convenient regeneration process. Nanomaterials are increasingly utilized for the elimination of various pollutants such as Carbon-based compounds, pathogenic microorganisms or toxins derived from living organisms, metal ions and arsenic from water (Al-Senani and Al-Fawzan, 2018). Carbon nanoparticles, including graphene, graphene oxide, fullerenes, carbon nanotubes, and activated carbons are extensively utilized in various fields including energy storage, sensors, electronics, and crude oil cleansing due to their remarkable mechanical, chemical, thermal, and electrical features.

Carbon Nanotubes (CNTs) have become widely recognized as an absorber among nanomaterial of carbon due to the distinctive chemical and physical characteristics they possess (Fu *et al.*, 2019). It is crucial to recognize that there are two main classifications of carbon nanotubes (CNTs): single-walled (SWCNTs) and multi-walled (MWCNTs). Over the past decade, carbon nanotubes (CNTs) have demonstrated significant potential for the crude oil cleansing, elimination of metallic cations and colourants (Farghali *et al.*, 2013).



This paper aims to synthesize carbon nanotubes (CNTs) and evaluate their potential for removing crude oil spills.

2.0 MATERIALS AND METHODS

2.1 Sample collection, identification and preparation

The coconut shell samples were obtained from Sokoto South Local Government Area of Sokoto State, Nigeria. Subsequently, the specimen was identified and the shells were thoroughly cleansed to eliminate any soil contaminants, then air-dried and ground into powder.

2.2 Synthesis of Carbon nanotubes

A 250 g of the powdered sample was placed in a muffled furnace and heated for six hours at 600 °C, which supposedly broke down sample into carbon, oxygen, and hydrogen species. The hydrogen species then flies away to form an embryonic cap, which is where subsequent CNT growth occurs (ASTM, 2018). After further dispersing 10 g of the pyrolyzed material in distilled water, it was centrifuged for 30 minutes at 11,000 rpm, and the solution containing the liquid portion was collected and stored at a temperature of 4 °C. The technique was repeated 15 times in order to attain a higher yield.

2.3 Characterization of Carbon Nanotubes

The synthesized carbon nanotubes were characterized using Fourier Transformed Infrared Spectroscopy (FTIR), Ultraviolet-Visible Spectroscopy (UV-Vis Spectroscopy), and Scanning Electron Microscopy (SEM).

2.4 Crude Oil Spills Removal Experiment

2.4.1 Preparation of Simulated Oil Spill

A quantity of 9.72 g of crude oil was introduced into 500.0 cm³ of brine water with a concentration of 0.003% weight of sodium chloride (NaCl), a typical small oil spill scenario with an initial concentration of 4.86 g/L was simulated. To create an emulsified solution, a mechanical shaker was used to agitate the immiscible solution for 15 minutes (Nwabanne and Igboke, 2012).

2.4.2 Batch Adsorption Dosages

The experimental study involved measuring 100 cm³ of the simulated oil spill, which had an initial concentration of 4.68 g/L, and placing it into a 500 cm³ beaker. Batch adsorption experiments were conducted to investigate the effects of two variables: (i) the amount of adsorbent used and (ii) the duration of contact time. The batch adsorption equilibrium studies were performed by measuring exactly 1.0 g of synthesized CNT into a 500 cm³ beaker containing the initial concentration of the simulated crude oil spill. To achieve equilibrium, the mixture was vigorously stirred in an orbital shaker at a speed of 200 rpm at a temperature of 25 °C for a duration of 30

minutes. The synthesized CNT that had been adsorbed was separated by filtration using a Whatmann filter paper (1) and a suction funnel. The remaining crude oil-in-water solution was then mixed vigorously using an orbital shaker for a duration of 15 minutes, resulting in the formation of an emulsified solution. The equilibrium concentration of the emulsified solution for each measured sample was calculated using a UV-Vis spectrophotometer at a specific wavelength of 380 nm. The experiment was replicated using 2.0, 3.0, 4.0, and 5.0 g of the substance, as described by Olufemi *et al.* (2014).

2.4.3 Contact Time

The batch adsorption experiment involved adding 5.0 g of synthesized CNT to a 500 cm³ beaker containing a simulated oil spill with an initial concentration of 4,680 mg/L. The mixture was then agitated in an orbital shaker at a speed of 200 rpm and a temperature of 25 °C for different contact times of 15, 30, 45, 60, and 120 minutes. Equation 1 was used to determine the amount of crude oil adsorbed per unit mass of activated carbon at equilibrium, *q_e* (mg/g), for each batch run.

$$q_e = \frac{C_o - C_e}{M} \times V \dots\dots\dots (1)$$

Equation 2 was used to get the amount of crude oil adsorbed per unit mass of activated carbon at time *t*, *q_t* (mg/g).

$$q_t = \frac{C_o - C_t}{M} \times V \dots\dots\dots (2)$$

Equation 3 was used to determine the percentage removal of crude oil.

$$\% \text{ removal of crude oil} = \frac{C_o - C_e}{C_o} \times 100\% \dots\dots\dots (3)$$

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Synthesized Carbon nanotubes

3.1.1 Fourier-transform infrared spectroscopy (FTIR)

FTIR is an invaluable method for characterizing carbon nanotubes (CNTs). FTIR is employed to quantify the absorption of infrared radiation, hence yielding insights into the functional groups and structural features.

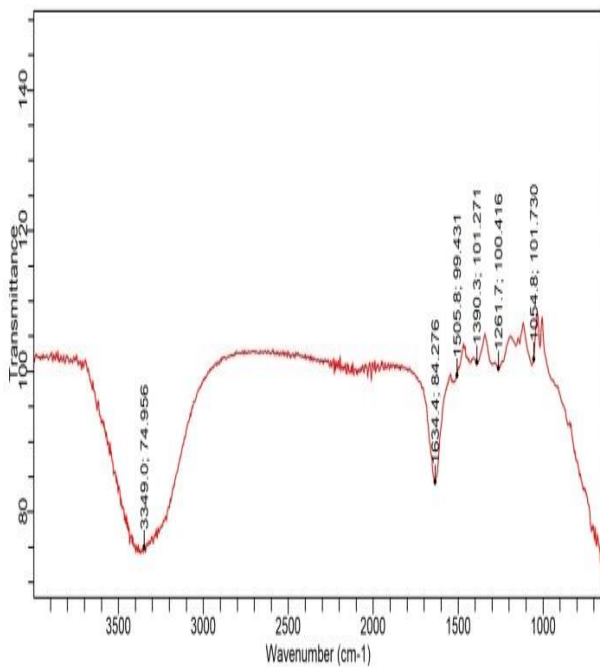


Fig. 1: FTIR of synthesized CNTs

The peaks seen in the range between 3349 cm^{-1} were attributed to the stretching of O-H bonds in alcohol compounds and the stretching of aldehyde-C-H bonds in alkanes. The peaks at 1262 cm^{-1} correspond to the medium C-N stretch vibration of amines, while the peaks at 1506 cm^{-1} relate to the C=C stretching of aromatics. The peak at 1055 cm^{-1} corresponds to the stretching of the C-O bond in a primary alcohol. The post-reaction analysis reveals that the displacement in the peak signifies the potential involvement of carboxyl, hydroxyl, and amide groups in the nanoparticle production process (Veerawamy and Ankur, 2020).

3.1.2 Uv-Vis Spectroscopy

Carbon nanotubes (CNTs) can be characterized using the UV-vis spectroscopy approach, which offers details on their optical characteristics and electronic structure (Mourdikoudis *et al.*, 2018). Transitions between the energy levels of the nanotubes are represented by the absorption peaks in the Uv-vis spectrum. Furthermore, the diameter and chirality of the CNT can be inferred from the intensity and shape of these peaks. The 200–500 nm range was used to get the results. A distinct signal that emerged from the synthetic CNT at 326.4 nm indicates that CNT is present.

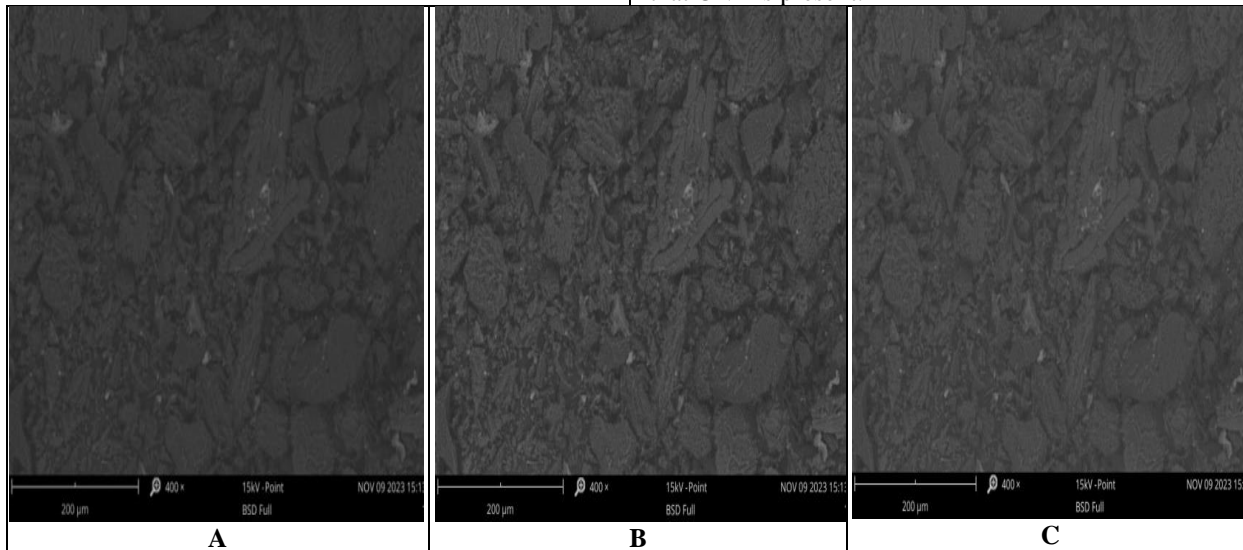


Fig. 2: A, B and C Scanning Electron Microscopy (SEM) of synthesized CNT

3.1.3 Scanning Electron Microscopy (SEM)

The produced CNT was found to have rough surfaces with variable form and size as well as tiny holes that resembled pores with an unequal porosity, according to scanning electron microscopy (SEM) data. The resultant structure's sharp edges show that the synthetic CNT has good crystallinity. SEM result produces high-resolution pictures that make it possible to observe the diameter, length, and shape of CNTs. This helps determine the unique identity of each nanotube and evaluate the structural integrity of each one.

3.2 Crude Oil Removal Experiment

3.2.1 Effect of Adsorbent Dosages

The impact of adsorbent dosage on the adsorption of crude oil was assessed by varying the amount of synthesized Carbon nanotubes (CNTs) employed as the adsorbent.

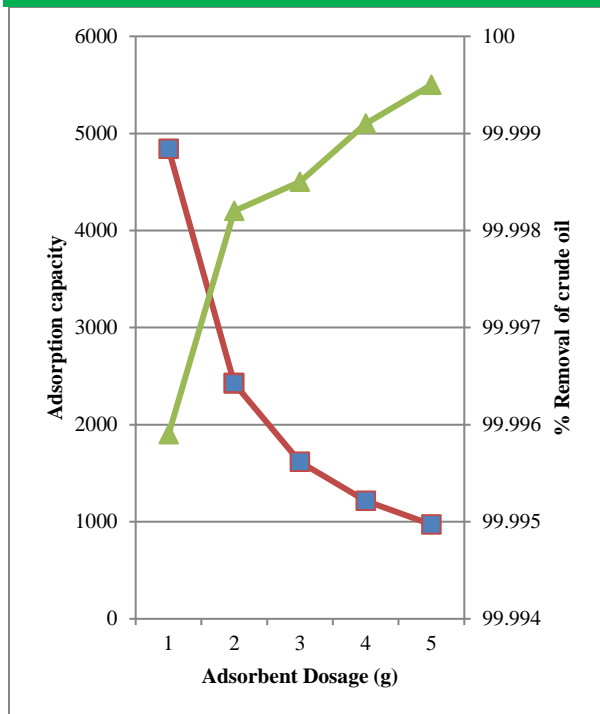


Fig. 3: Effect of adsorbents dosage on the adsorption of crude oil

Based on fig. 3, the use of additional adsorbent leads to a decrease in the adsorption capacity of the adsorbent, but the percentage of crude oil extracted increases. The augmented number of active sites on the surfaces of the synthesized CNT led to an enhanced adsorption of crude oil when a greater quantity of adsorbent was employed. Nevertheless, this also resulted in a reduction in the adsorption capacity of crude oil per unit mass of adsorbent due to the increased presence of unsaturated adsorption sites during the adsorption process (Babiker and Mohamed, 2022).

With a limited quantity of adsorbent, several active sites were present on the surface of the synthesized CNT, facilitating the interaction between the crude oil and the adsorbent. As a result, more crude oil molecules were able to occupy these active sites on the surface of the adsorbent. This led to a high adsorption capacity of 4840.0 mg/g and a percentage removal of crude oil of 99.99%. In contrast, as the amount of adsorbent used was raised, there was an insufficient number of active adsorption sites available to accept the crude oil molecules. Consequently, this resulted in a reduced adsorption capacity of 971.5 mg/g and a higher percentage of crude oil removal, reaching 99.99%. When a large volume of adsorbent was used, the oil covered the surface of the sorbent quickly, resulting in rapid saturation and leaving behind a significant quantity of unattached oil (Yang *et al.*, 2019).

3.2.2 Effect of Contact Time

The impact of contact duration on the adsorption of crude oil was assessed by employing various contact times for an equivalent mass of synthesized CNT.

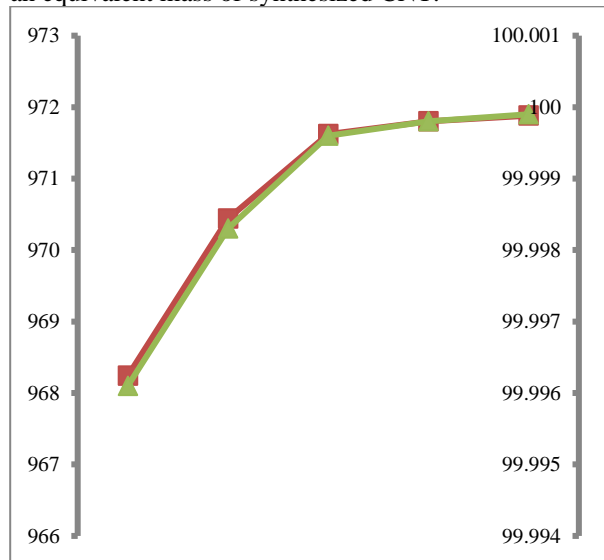


Fig. 4: Effect of contact time on the adsorption of crude oil

In accordance to fig. 4, the process of crude oil being absorbed onto the synthesized CNT was found to be fast during the first 15 to 30 minutes of contact time. After that, the absorption continued at a slower pace until it reached a point of saturation at 45 minutes. The initial high absorption capacity and the percentage of crude oil removal can be attributed to the existence of unoccupied active sites on the surface of the synthesized CNT, as well as the reduction in the strong attractive forces among the crude oil molecules and the surface of the adsorbent as the contact time increased (Supriya *et al.*, 2019).

After 45 minutes, it was noted that the adsorption capacity and percentage of crude oil removal remained unchanged. This is likely because the surface of the synthesized CNT became saturated with crude oil particles, and a balance was reached between the adsorption and desorption processes that occurred after saturation (Cai *et al.*, 2019). The synthesized carbon nanotubes (CNT) exhibited a remarkable adsorption capacity of 971.88 mg/g and achieved a crude oil removal rate of 99.99%. This exceptional performance can be attributed to the CNT's extensive surface area, which facilitates rapid diffusion of crude oil onto the external material surface. Subsequently, there is swift pore diffusion into the intra-particle matrix until equilibrium is reached within 120 minutes (Cai *et al.*, 2019). As such carbon nanotubes is one approach capable of rapidly reducing pollutant (Boregowda *et al.*, 2022). The approach is economically efficient since it minimizes the



requirement to transport the polluted crude oil for most of the remediation procedure. Furthermore, nanomaterial have the capability to be recycled and repurposed for the remediation of environmental contaminants (Sathish *et al.*, 2024).

4.0 CONCLUSION

The synthesized carbon nanotubes (CNT) were analyzed using FTIR, Uv-Vis, and SEM techniques. The results revealed that the synthesized carbon nanotubes (CNTs) are in the nano range and possess a high surface area to mass ratio, suggesting excellent crystallinity. The morphological alteration greatly enhanced the hydrophobic nature of the adsorbent, resulting in the synthesis of a carbon nanotube (CNT) with much improved capacity for adsorbing and removing crude oil. The experimental results demonstrated a positive direct correlation between the increasing dosage of adsorbent and the percentage of crude oil removal. Similarly, an increase in contact duration also resulted in a higher percentage of crude oil removal. Carbon nanotubes synthesized, offer an excellent structure for effectively purifying contaminated crude oil.

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