

Effect of Crude Oil Sorption Capacity on Raw and Modified Coir Fibre

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ABSTRACT

A critical need for a more sustainable approach to oil spill cleanup in Nigeria, especially the Niger Delta, was highlighted by the environmental and economic devastation documented in the 2011 United Nations Environment Programme (UNEP) assessment of Ogoni land. Existing cleanup methods relying on synthetic sorbents proved expensive, logistically challenging, and harmful to the environment due to their non-biodegradable nature. This research investigated the potential of natural coir fibers, a readily available and low-cost resource in Nigeria, as an alternative. The inherent advantages of coir, such as low density, appropriate stiffness, disposability, and renewability, make it a promising candidate. The research explored modifying coir fibers through acetylation to improve their oil absorption and reusability. Sorption experiments and oil recovery assessments were conducted to evaluate the effectiveness of the modified coir sorbent. Additionally, FT-IR, XRD, and TGA analyses were employed to understand the material properties and the impact of the treatment. Overall, this research provides valuable insights into the potential of utilizing natural coir fibers as a sustainable solution for oil spill cleanup in Nigeria.

Keywords: Crude oil, coir fibre, oil sorption, hydrophobicity

INTRODUCTION

An oil spill releases a liquid petroleum hydrocarbon into the environment, especially the marine ecosystem, due to human activity, and is a form of pollution. The term is usually given to marine oil spills, where oil is released into the ocean or coastal waters, but spills may also occur on land. Oil spills may be due to releases of crude oil from tankers, offshore platforms, drilling rigs and wells, as well as spills of refined petroleum products (such as gasoline, and diesel) and their by-products, heavier fuels used by large ships such as bunker fuel, or the spill of any oily refuse. Oil spills cause environmental pollution thereby contaminating the physical and biological components of the earth/atmosphere system to such an extent that normal environmental processes are adversely affected (Ivshina., 2015).

Various natural processes affect petroleum and refined products after they are spilled into the environment (Figure 1). Depending on their chemical and physical characteristics, various hydrocarbon fractions will selectively evaporate, spread over the surface, dissolve into water, accumulate as persistent residues, or be degraded by microorganisms and solar ultraviolet radiation.

Crude oil is the major source of revenue in Nigeria with the vast majority of exploration from the Niger Delta. Delta region of Nigeria has about 606 oil fields with 355 situated onshore; 251 situated offshore with 5284 drilled oil wells and 7,000 km of oil and gas pipelines (Anifowose, 2008; Onuoha, 2008). Activities of the oil industry are widespread across the length and breadth of the region (Figure 2).

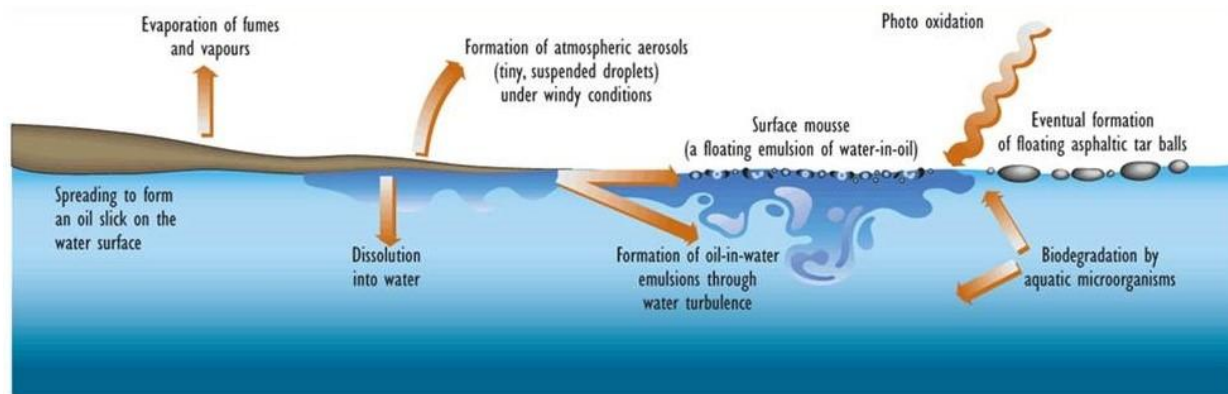
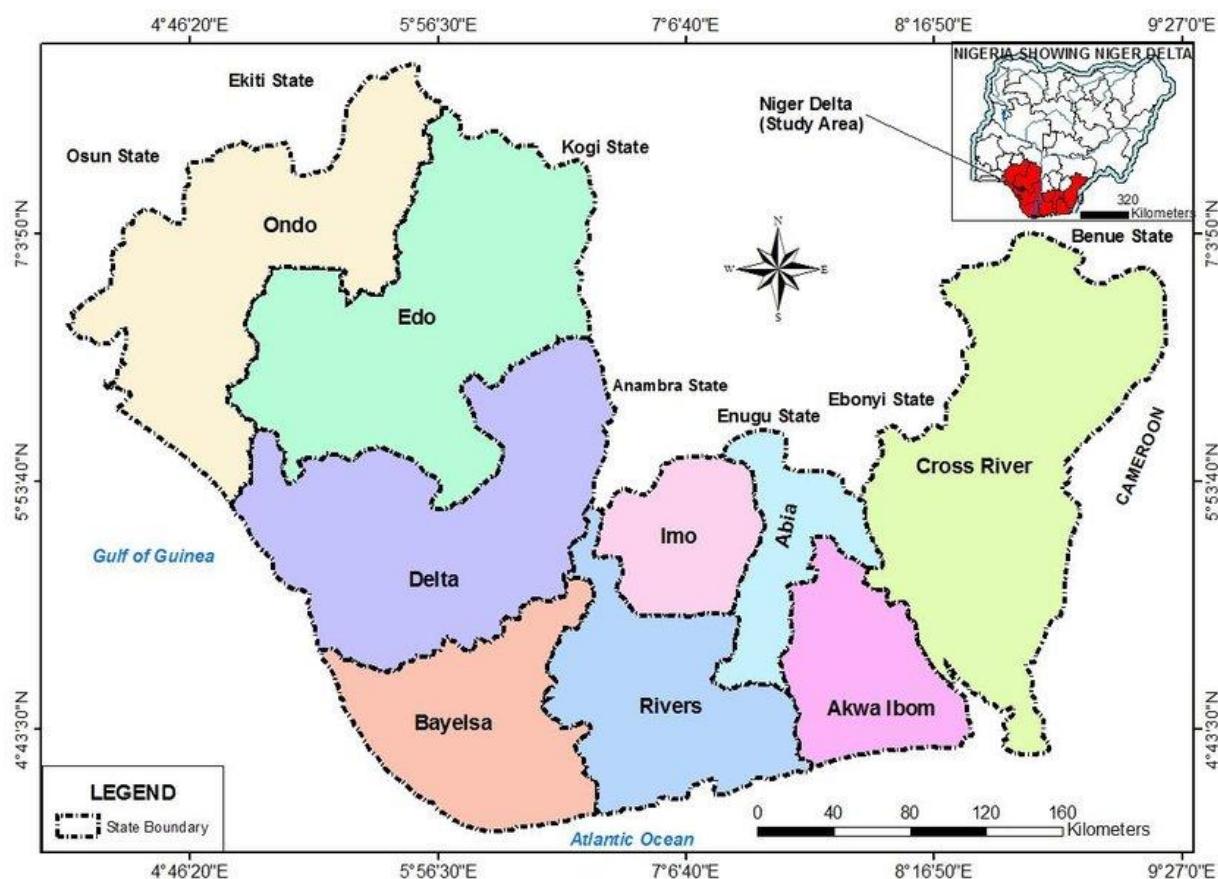


Fig. 1: Fate of Spilled Petroleum on Water. Source: Modified from Clark and MacLeod (1977).



Map of Niger Delta Region Showing the 9 states of the oil-rich region. Inset: Map of Nigeria showing position of Niger Delta Region.

Cleanup and recovery from an oil spill is difficult and depend upon many factors, including the type of oil spilled, the temperature of the water (affecting evaporation and biodegradation), and the types of shorelines and beaches involved. Spills may take weeks, months or even years to clean up. Oil spills can have disastrous consequences for society; economically, environmentally, and socially. As a result, oil spill accidents have initiated intense media attention and political uproar, bringing many together in a political struggle concerning government response to oil spills and what actions can best prevent them from happening (Wout, 2015). Crude oil and refined fuel spills from tanker ship accidents have damaged vulnerable ecosystems in Alaska, the Gulf of Mexico, the Galapagos Islands, France, the Sundarbans, the Ogoni land, Nigeria and many other places. The quantity of oil spilled during accidents has ranged from a few hundred tons to several hundred thousand tons (e.g., Deepwater Horizon Oil Spill, Atlantic Empress, Amoco Cadiz), but volume is a limited measure of damage or impact. Smaller spills have already proven to have a great impact on ecosystems, such as the Exxon Valdez oil spill

because of the remoteness of the site or the difficulty of an emergency environmental response (David, 2015).

Many techniques have been devised to combat this problem. These techniques include in-situ burning, bioremediation, chemical dispersion and synthetic sorbents in spite of their secondary effect of non-degradability (Singh *et al.*, 2014). The most widely accepted by many researchers and industries is the one prepared from polypropylene fibres and is now being considered hazardous (Wei *et al.*, 2003; Yuan and Chung, 2012; Bayat *et al.*, 2005). Nanocellulose aerogel, carbon nanotubes are the recent ones that gave high absorbency capacity (g/g), but these cannot be sustained because of the high cost of raw materials and processing (Gui *et al.*, 2010; Korhonen *et al.*, 2011; Wahi *et al.*, 2013; Al-Majed *et al.*, 2012). Most recent research discovery shows that natural materials are the best for oil cleaning-up (Singh *et al.*, 2014). Moreover, cotton and kapok are the best amongst the greens. This was because of their higher oil sorption capacity, biodegradability and recyclability. Hence, they are prominent materials for oil spill

cleanup. Cotton are loose fibres, which presumably limited their application (Singh *et al.*, 2014). The problem with cotton necessitated the use of modified natural fibres to enhance their oleophilicity as reported by Teli and Valia (2013; 2014; 2015; 2016) that modified coir and jute fibres are of low cost and high-capacity effective oil sorbents. Oil sorbents play a very important part in the remediation processes of oil spills. To enhance the oil-sorption properties and simplify the oil-recovery process, various advanced oil sorbents and oil-collecting devices based on them have been proposed recently. Although numerous advanced oil sorbents and oil-sorbents based oil-collecting devices have been successfully developed, there are some crucial issues that need further exploration in this active research field in the future.

The disposal of oil-soaked sorbents is still a great challenge. Presently, various methods have been proposed for the recovery of oil sorbents and the absorbed oil from oil sorbents for reuse, these methods are still not efficient and economical enough. Besides the oil re-leakage problem caused by the rebleeding of absorbed oil from the sorbents under external forces, air pollution caused by the evaporation of absorbed oil inside the sorbents is still a crucial issue for researchers to settle. All in all, much challenging work is still in front of us for the fabrication of next-generation oil-sorbent materials, oil-collecting devices based on oil sorbents, and recycling of both oils and sorbent materials. (Ge *et al.*, 2016). Hence, this research is focus on the use of coir fibre for oil spill cleanup, while, mechanical oil-recovery method will be use to collect the sorbed oil for reuse.

MATERIALS AND METHODS

Materials

Coir fibres was purchased from Railway Market, Kaduna, and National Research Institute of Chemical Technology (NARICT), Zaria, Kaduna State, Nigeria. Acetic anhydride Sigma Aldrich M = 102.09, 11.080 Kg and N-Bromo Succinimide (NBS) - BDH-Idiometric 90%. 100 g- were purchased from Zayo Sigma Aldrich, Paderborn-Elsen, Germany, Crude oil samples were obtained from Research Laboratory, of Nigeria Petroleum Development Company (NPDC) a subsidiary of Nigeria National Petroleum Company (NNPCL), Warri Delta State, Nigeria.

Methods

Preparation of coir fibre

Coir fibre were extracted from the pulp husks surrounding the coconut manually. The extracted fibres were severally washed in water, followed by drying, removing of impurities, separation, sorting and mixing. The water residue was tested using litmus paper which indicates neutrality. Hence, the coir fibres extracted do not add any toxicity to fresh laboratory water. The extracted coir fibres after drying were brown in colour and the length ranges from 5 - 7cm indicating that they are recovered from ripe coconut husks as distinct feature of matured coconut husk extracted fibre. The fibre is bristle, the length of the fibres falls within 10-30 cm. The extracted fibres after removal of impurities and sorting by removing short fibres below 5 cm were done manually. The sorted fibres were mixed manually to obtain a suitable composition. Finally, the mixed fibres were dried at 60 °C for 16 hours in an oven as described by Sun *et al.* (2002).

Acetylation of coir fibre

Coir fibres were modified by acetylation in solvent free system, 50 g of coir was placed in 1000 ml round bottom flask containing acetic anhydride (1:20) and NBS (1%) as a catalyst. The flask was then placed in water bath set at 90°C using atmospheric pressure with reflux condenser fitted. The reaction was continued for 1hr at 90°C in water bath as shown in Plate 1, then the flask was removed from the oil bath and the hot reagent decanted off. The acetylated fibres were then thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid bye products. The modified fabric was dried in oven at 60°C to constant weight.

Oil sorption capacity

Oil sorption capacity was determined by using the method reported in literature by Sun *et al.* (2004). A fixed quantity of crude oil was in this experiment (100 g) was suspended in water in a beaker the modified coir fibre 2 g was added to at room temperature and allowed to absorb oil for 1 hr. The modified fibre sample then removed and held to drain off the excess amount of oil. The fibre sample was then reweighed to determine the absorptivity (Sun *et al.*, 2004).

Recovery of crude oil sorbed and reusability of sorbents

Pad mangle machine was used at a pressure of 40 Pa was used, the sorbed sample was weighed and then squeezed between the two rollers and the crude oil recovered was weighed to determine the

amount of recovered oil. While the squeezed was also weighed sample. This cycle was further repeated to determine the amount of oil sorbed during each cycle

FT-IR

FTIR Agilent Technology for the modified and acetylated jute fabric was used from multipurpose laboratory, Department of chemistry, Ahmadu Bello University, Zaria. Changes in chemical properties were observed with FT-IR spectroscopy on PP and glass fiber-reinforced PP pellets using ASTM E1252- 98 (2013). The result spectra were recorded using an FTIR spectrometer (Perkin Elmer Spectrum 400, model Perkin Elmer Inc., USA) using resolution of 4 cm^{-1} over 20 scans. The scans were done in transmittance mode within a $4000\text{--}500\text{ cm}^{-1}$ range

X-ray diffraction (XRD)

X-ray diffraction analysis was carried out using X-ray machine at Federal University of Science and Technology (FUT), Minna, using X-ray diffractometer. The sample was analysed using the reflection-transmission spinner stage using the Theta-Theta settings. Two-Theta starting position was 4 degrees and ends at 75 degrees with a two-theta step of 0.026261 at 8.67 seconds per step. Tube current was 40 mA and the tension was 45VA. A Programmable Divergent slit was used with a 5 mm width mask and the Gonio Scan was used.

Thermogravimetry (TGA) analysis and differential thermal (DTA) analysis

DTA plots recorded the temperature difference between a sample and a reference than the heat properties of material. The sorbents here were subjected to abreast the heat properties that involved in the transitional changes e.g., crystalline, melting, glass etc. The crystallinity and amorphous intensities are considered in this study. DTG-DTA PerkinElmer machine with “Pyris” software manager at Federal University of Science and Technology (FUT), Minna, was used for the analysis. The TGA Heat measurement conditions were from 30°C – 950°C at $10.00^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSIONS

Absorption range at 1718.3 cm^{-1} for FTIR of the modified coir fibre indicates that modification has occurred with decrease of intensity from 3280.1 cm^{-1} to 3343.4 cm^{-1} of the O-H group assigned to cellulose decreasing significantly. Hence, enhancement of the character of the coir fibre.

Figures 3 and 4 show the FTIR spectrum of the unmodified and modified acetylated coir fibre respectively.

Furthermore, the results confirmed the esterification of cellulose hydroxyl group with acetic anhydride. A clear evidence of esterification reaction is observed by emergence of a new ester carbonyl band. The FT-IR analysis also confirmed the enhancement of the hydrophobic character of the cellulose fibres after esterification with the acetic anhydride and the intensity of the band, at around 1509 cm^{-1} , assigned to absorb water molecules, decrease significantly. Surely and indeed this band is almost completely absent in the IR spectra of the modified coir fibre. Hence, enhancement of the character of the coir fibre. Similar results have been reported (Sun *et al.* 2004; Sun *et al.*, 2002; Teli *et al.*, 2016; Teli *et al.*, 2013).

TGA-DTA analysis. Figures 3 and 4 illustrate the superimposed thermograms of unmodified and modified coir fibre, DTA and TGA studies in the temperature ranging ambient temperature to 800°C at a rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen flow. It was deduced that in an onset stage of the thermogram, ranging from ambient temperature to about 150°C , first endothermic peak was observed, resulting to weight loss caused by dehydration and pyrolysis process in the sorbents. In the initial stage weight loss of raw and acetylated fibres of both fibres were relatively low, samples gave an initial decrease of below 100°C due to loss of moisture (see W).

In the figures 5 and 6, the raw coir and weight start to decompose at 280°C , 245°C respectively, whereas the modified acetylated coir fibres starts to decompose at 215°C , 265°C respectively, (see X) in the thermograms. At 50% weight loss the decomposition temperature occurs for raw coir fibre at 375°C , for the acetylated coir fibres at 420°C respectively after (Y) and before (Z), where the plots TGA/DTA intercept.

This increasing trend of decomposition temperature indicated that the thermal stability of the acetylated coir fibres are higher than that of the unmodified fibres with coir fibre. Similar trend was reported by Sun *et al.* (2002) for rice straw. However, for temperatures beyond 500°C (after Z) in all cases, the weight loss was steady and slow and this clearly indicates that the acetylated fibres showed relatively lower thermal stability as compared with raw fibres.

The conceivable reason could be that there are disintegration of intermolecular interactions such

as hydrogen bonds between polymer molecules as a result of acetylation (Hill et al., 1998).

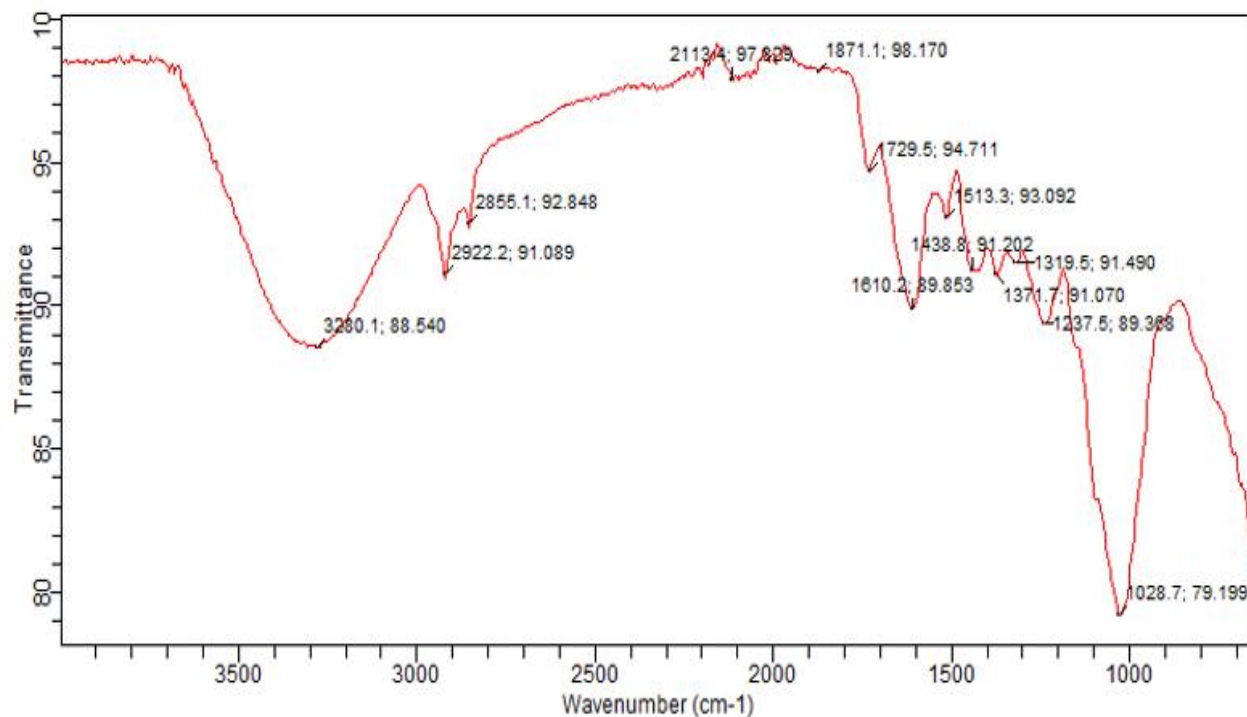


Fig. 3: FTIR Spectrum of unmodified coir fibre

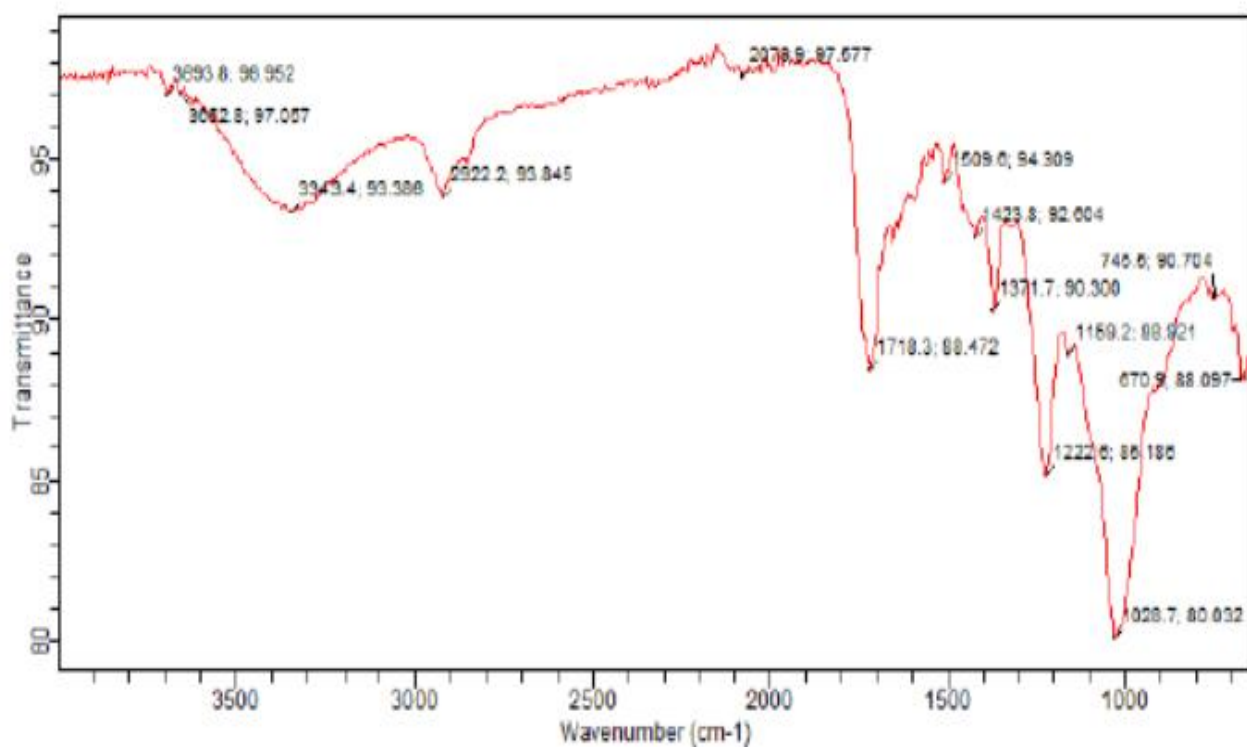


Fig. 4: FTIR Spectrum of unmodified coir fibre

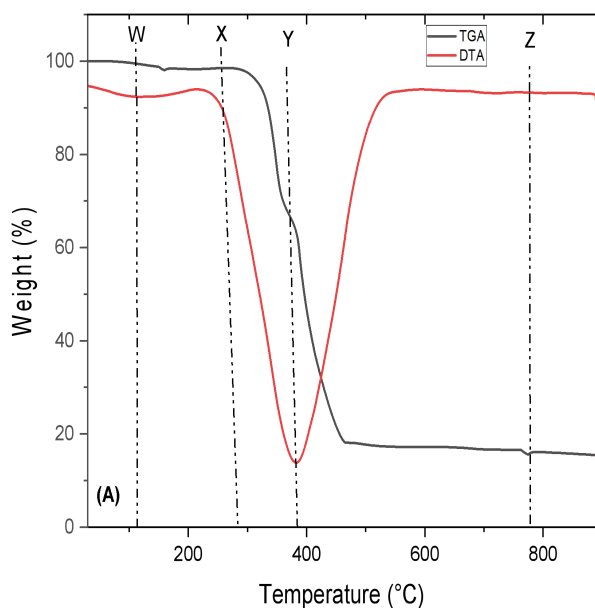


Figure 5: Unmodified coir fibre Superimposed TGA-DTA

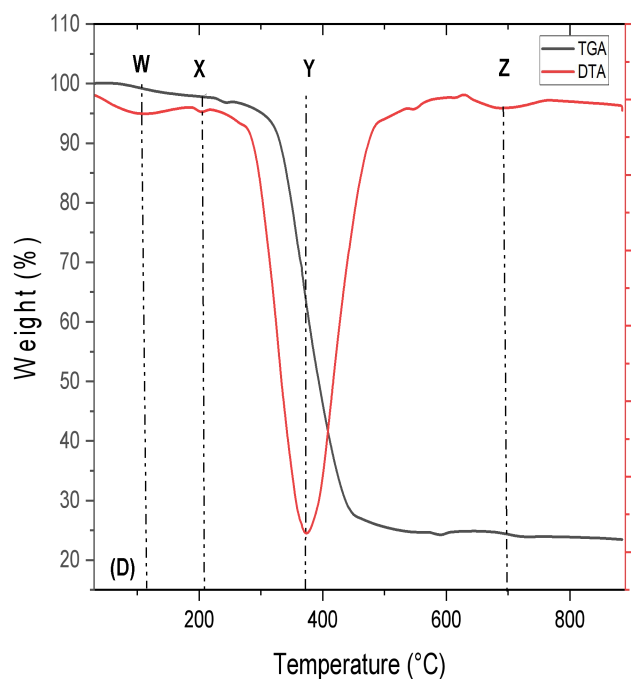


Figure 6: Modified coir fibre Superimposed TGA-DTA

CONCLUSION

The modification of coir fibre by acetylation method with acetic anhydride has imparted hydrophobic properties to the fibre. The acetylated coir fibre had very little affinity for water and strong affinity for oil. Hence, the modified coir fibre would be suitable for application as an oil sorbent material for oil spill cleanup. Furthermore, coir fibre being natural and biodegradable, its disposal after use would be easy. Therefore, it will not cause any environmental pollution.

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