



# EFFECT OF SURFACE MODIFICATION ON THE SORPTION CAPACITY OF *Piliostigma reticulatum* AS A SORBENT FOR CRUDE OIL REMOVAL FROM WATER



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Received: March 30, 2021 Accepted: May 18, 2021

**Abstract:** The need to seek inexpensive, abundant and effective materials as oil spill sorbents in water has focus on natural organic sorbents mainly from agricultural products. This study explored the used of crude *Piliostigma reticulatum* (CPR), retted *Piliostigma reticulatum* (RPR), bleached *Piliostigma reticulatum* (PFPR) fiber as sorbent for crude oil removal from water. Sorption capacity studies was carried and optimization at various condition. The results revealed that the efficiency of sorbent to remove crude oil from water is related to the sorbent weight, contact time, initial oil concentration and temperature of sorption. RPR with the highest sorption capacity of 7.92 g/g at 0.7 g of the sorbent was selected and modified through acetylation, succinylation in ionic liquid, silanylation and salt treatment. The functional groups involved in oil sorption were identified via the determination of the chemical structure of the sorbents before and after oil sorption. Change in the spectral peaks of the sorbents after absorption of crude oil at wave number 2922. 3 cm<sup>-1</sup> corresponding to -CH alkane stretching, can be attributed to addition of crude oil. The SEM images show some wrinkles and roughness on the surface of the pretreated and modified sorbents. The elemental composition of the sorbent before treatment and after treatment reveals a reduction in oxygen availability as evidenced by the decrease in peak height of oxygen signal. The sorption capacity of the modified sorbent was compared to that of the pretreated sorbent RPR, to check the sorption capacity after chemical treatment. 0.3 g of the sorbent was used with contact of 20 min at initial oil concentration of 10 g/mL at temperature of 30°C. RPR has the least oil removal capacity of 5.69 g/g, compared to ACT-PR (7.79 g/g), SIL-PR (7.70 g/g), SUC-PR (6.84 g/g) and ZN-PR (9.31 g/g). Surface-modified sorbent has noticeable high oil sorption capacity compared with the retted sorbent. RPR attained its highest sorption capacity of 7.92 g/g at 0.7g of the sorbent weight, while ACT-PR, SIL-PR, SUC-PR, ZN-PR attained the highest sorption capacity of 10.51, 10.12, 8.52 and 11.05 g/g at 0.5 g of the sorbent weight after optimization. The sorbent exhibited good reusability after 8 cycles and RPR, ACT-PR, SIL-PR, SUC-PR and ZN-PR losses 33, 18, 17, 22 and 16%, respectively of the initial adsorb oil showing good retention capacity. Effective replacements of hydrophilic hydroxyl groups of fibers by the hydrophobic groups during modification improves its the affinity toward oil.

**Keywords:** *Piliostigma reticulatum*, modification, sorption, crude oil, sorbent

## Introduction

One of the most abundant natural resources on earth is water but only about 1% of that resource is available for human consumption. Over 1.1 billion people are estimated to lack adequate supply of drinking water due to the rising cost of potable water, growing populations, and variety of climatic and environmental concerns (Adeleye *et al.*, 2016; WHO, 2015). The major challenge in water supply chain is the continuous contamination of fresh water resources by a variety of organic and inorganic pollutants. The estimated world population of 7.6 billion is placing increasing pressure on the world's limited water resources while more water is being consumed, the quality of water is declining due to the significant amounts of pollutants being discarded into the world's river systems, lakes and oceans each day (Rahman *et al.*, 2018).

Many raw materials for the production of chemical and synthetic polymers are derived from oils (Almeida *et al.*, 2019). Globalization has become a major cause of reliance on oil energy, and the use of such oils continuously pollutes the environment. Oil is considered a source of energy in various industrial applications worldwide. Oil spillage is a threat because of the contamination of water bodies. Oil spill pollution is one of the most hazardous water quality degradation due to human activities, affecting aquatic ecosystems. Increased in the number of accidents and oil leakages has led to the continuous improvement of oil spill cleaning techniques in order to address and minimizing their disastrous effects. The result of crude oil activities leaves most of our surface waters heavily contaminated with several pollutants including dissolved and dispersed oils. These pollutants pose threat to our aquatic life and make our soil

infertile (Muhammad *et al.*, 2015; Golam *et al.*, 2018). To protect the water and the environment, this oil should be removed from the water or the surface (Zamparas *et al.*, 2020; Wolok *et al.*, 2020).

The treatment of wastewater and drinking water can reduce these concerns however, the traditional methods of treatment are not efficient enough to completely remove the emerging contaminants and meet the strict water quality standards (Anjum *et al.*, 2016). Effective decontamination and clean-up are necessary after a spill for the protection of the environment and human health (Nwadiogbu *et al.*, 2016; Xu *et al.*, 2019). Sorbent materials remove oil by two mechanisms. These can either be done by adsorption or absorption. Adsorption involves the adherence of oil to the sorbent material while, absorption relies on capillary attraction; oil fills the pores within the material and moves upward (uptake) into the material due to capillary force. Sorbent can be grouped as inorganic minerals and synthetic, organic, and organic (agricultural) products. Agricultural sorbents are cheap, efficient, environmentally friendly, and easy to deploy (Idris *et al.*, 2014).

Natural fibers have been shown to have many advantageous properties for oil remediation work; in particular, such materials are biodegradable, renewable and low in cost. Natural fibers have attracted a broad interest in current research on hydrophobic treatments, and exemplary studies have focused on oil-adsorption materials such as, cotton (Wang *et al.*, 2015), pomelo peel (Zou *et al.*, 2015), sugarcane bagasse (Boni *et al.*, 2016). Agricultural waste sorbents such as empty fruit oil palm bunch (*Elaeis guineensis*) and cocoa pods are abundantly available in different parts of Nigeria (Onwuka *et al.*, 2018). Natural fibers show commendable oil-

absorbing performance, with potentially wide applications (Lv *et al.*, 2017). Several authors, in the last few years have taken into consideration the possibility to using natural fibers to remediate water polluted by oil. Experiments have been done using sugarcane bagasse with removal efficiency up to 70% (El-Gendy and Hussein, 2016), straw-peat composite (Paulauskiene and Jucike, 2015), other agriculture wastes such as rice straw (Younis *et al.*, 2014), activated rice husk (Yakout and Daifullah, 2013), naturally hydrophobic cellulose such as unprocessed cotton, kapok, or milkweed seed hair and, in addition, a wide assortment of activated cellulosic materials (Hubbe *et al.*, 2013).

The plant *Piliostigma reticulatum* (DC) Hoechst is an evergreen shrub or small tree with a twisted bole widely distributed in Northern, Western and Eastern Africa. It is reported to possess medicinal properties similar to *Piliostigma thonningii*. A fiber obtained from the bark is used to make clothes and rope. Plant-derived sorbents have excellent adsorption capacity, biodegradability and non-toxicity in comparison with synthetic sorbents, but their low hydrophobicity increases water uptake and lowers oil sorption capacity. To address this drawback, the hydrophobicity of fibres is usually enhanced by chemical modification. Many researchers are therefore working on the enhancement of oil sorption affinity through various modifications or the addition of hydrophobic moieties to these natural sorbents, as the functional group properties play a significant role in the adsorption of oils (Doshi *et al.*, 2018; Khalid *et al.*, 2018).

The effectiveness of the sorbents in saturated environments can be enhanced when the density of the hydroxyl functionalities is decreased. The hydroxyl functionality of these fibers can be reduced by chemical modification, such as mercerization, acetylation, succinoylation, silanylation and addition of salts. In the last decade, there have been many major oil spills that have resulted in considerable environmental damage despite clean-up efforts. Therefore, more work is needed to discover more available materials for oil spill removal on the surface of water. This study addresses characterization and modification of *Piliostigma reticulatum* as sorbent for removal of crude oil in water to enhance its usability as sorption material.

## Materials and Methods

### Sample collection and sorbent preparation

The fibrous plant *Piliostigma reticulatum* was collected from a farmland located in Girei Local Government Area, Adamawa State, Nigeria and identified by a Botanist from Modibbo Adama University of Technology, Yola. The plant part obtained was cut from the stem with a knife, the bark removed and washed with distilled water. It was spread on a clean polyethylene and allowed to dry in the laboratory for one week.

### Extraction of fiber procedure

The fiber was extracted from the fibrous plant stem using chemical retting extraction process, giving fiber of different lengths and diameters. The fibrous plant (Sample) was treated with 6% NaOH solution in accordance with work done by Cai *et al.* (2016). 15 g of the sample was submerged in 6% NaOH solution and heated at 100°C for 30 min in a water-bath. The fiber was rinsed in cold water to free fibers strands. It was neutralized with acetic acid and washed with distilled water repeatedly until all sodium hydroxide is eliminated. Finally, the fiber was dried at room temperature for 48 h.

### Bleaching of fibers

Retted fibers were scoured in 2% NaOH solution at 100°C for 30 min. Scouring of the fiber was carried out before bleaching. Dry scoured fibers were measured and submerged in a solution of 3% H<sub>2</sub>O<sub>2</sub>, with sodium pyrophosphate/sodium

oxalate as buffering medium at 55°C for 30 min to remove any colouring matter and white fibers was obtained.

### Characterization of crude oil sample

The properties of crude oil sample (COS) was characterized according to the method describe by Nwabueze *et al.* (2015). The density, viscosity, specific gravity and API gravity of the crude oil sample was investigated.

**1. Density:** The density of COS sample was taken by using a specific gravity bottle. The bottle was filled with oil and weighed at room temperature (28 – 30°C) and the density calculated from:

$$\text{Density} = \frac{(MS - Mb)}{Vb} \text{-----Eq. 1}$$

**Where:** MS = mass of oil plus bottle; Mb = mass of bottle; Vb = volume of bottle

The method was repeated in triplicate to obtain a mean value.

**2. Viscosity:** The viscosity for crude oil sample was determined using viscometer. The viscometer was cleansed with a non-toxic solvent and dried. A certain amount of crude oil sample was poured into a beaker, and then transferred to the viscometer. The viscometer was inserted into the water bath at the required temperature and the viscosity was recorded in poise and converted to centistokes. This was carried out in triplicate to obtain a mean value.

**3. Specific gravity:** The specific gravity of crude oil was determined from the results obtained for density. The specific gravity, being a more standard measurement was obtained by multiplying the density calculated with density of water 0.998 g/cm<sup>3</sup>.

### 4. American petroleum institute (API) gravity

The API gravity was calculated using the formula:

$$\text{API} = (141/s.g) - 131.5 \text{-----Eq. 2}$$

**Where** s.g = specific gravity of crude oil calculated.

### Characterization of crude fibers

The physiochemical properties of the sorbents will be investigated according to the method described by Donatus *et al.* (2015). All the following physiochemical properties were determined: Moisture Content, Ash Content, Volatile Content, Fixed Carbon, Density, Specific Gravity and Swell ability.

### Evaluation of oil sorption capacities

#### Test for oil sorption capacity by sorbent

The crude, retted and pure fibers were subjected to sorption studies to evaluate their sorption capacity. Factors that affect oil adsorption were investigated, namely the effect of variation in sorbent weight, contact time, oil concentration and temperature in water/oil medium and in oil medium. Tests were carried out at room temperature. The crude, retted and pure fibers were subjected to sorption studies to optimize the sorption properties. The methods describe by Onwuka *et al.* (2018) was adopted for the sorption studies. To simulate the situation of oil spill and minimize experimental variation, the crude oil sample was held in beakers for 1 day in open air to release volatile hydrocarbon contents. To 100 ml of distilled water in a 250-ml beaker, 10 g of crude oil was added. A portion 0.10 g of the sorbent was added into the mixture in the beaker and left unperturbed for 30 min. After 30 min, the sorbent was removed using a spatula and placed on sieving net and left to drain by hanging the net over a beaker for 10 min. The drained sample was weighed and recorded. This was repeated at different weights of 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g and results recorded. This experiment was also conducted at different times of 10, 20, 30, 40, 50, 60 and 70 min at constant sorbent weight/ oil concentration and results were recorded. The effect of Initial concentrations of crude oil was also studied from 5, 7.5, 10, 12.5, 15, 17.5 and 20 g/100 ml of water at constant sorbent weight and time and results recorded. The effect of temperature on sorption was

also investigated at different temperature (30, 35, 40, 45, 50, 55 and 60°C) at constant weight of sorbent and time. This was also repeated in oil medium. The sorption capacity of the sorbent samples was calculated using the expression:

$$\text{Oil sorption capacity} = \frac{\text{New weight gain}}{\text{original weight}} \text{ g/g} \text{ ----- Eq. 3}$$

and recorded as gram per gram of sorbent. The procedure was carried out in triplicates and the mean of the results reported.

#### Chemical modification of fibers

The sorbent with the highest sorption capacity above was functionalized by chemical modifications. The hydroxyl functionality of these fibers can be reduced by chemical modification of the selected sorbent by Acetylation, succinoylation in ionic liquid, silanylation and salt treatment.

#### Pre-treatment

The fiber undergoes scouring using an aqueous solution containing 2 wt% of sodium hydroxide for 1 h at 35°C to allow chemical reagents to penetrate the cellulosic fibers more easily while preserving the chemical composition of the fibers. The fibers were washed with tap water until pH $\approx$ 7 and left to dry for 24 h at room temperature before modification with other chemicals (Aaditan and Jahan, 2018).

#### Acetic anhydride treatment (Acetylation)

A calculated amount of fiber was placed in a 500-mL two-necked round bottom flask containing acetic anhydride (solid to liquid ratio, 1 g/30 mL) and *N*-bromosuccinimide (NBS) 3% as the reaction catalyst under atmospheric pressure. A reflux condenser, a thermometer, and a mechanical stirrer was attached to the flask. The flask then placed in an oil bath set to 120°C for 4 h. The flask was removed from the oil bath after the required time, the mixture inside the flask was decanted, and the fibers was thoroughly washed with acetone to remove unreacted acetic anhydride and acetic acid by-products. The modified fibers were placed in an oven at 80°C overnight and weighed to evaluate the WPG. The modified fibers were cooled in a desiccator and stored in a plastic container prior to analysis and crude oil sorption studies (Asadpour *et al.*, 2016; onwuka *et al.*, 2016).

#### Succinoylation in ionic liquid

This was carried out according to the method describe by Xin *et al.* (2017) and Shang *et al.* (2016). The succinylated cellulosic derivatives containing free carboxylic groups was prepared by homogeneous reaction of sorbent with a catalysts *N*-bromosuccinimide (NBS), Triethyl pentyl phosphonium bis (trifluoromethyl sulfonyl) imide (ionic liquid) in the solvent system containing DMSO. Dried sorbent was added to ionic liquid (IL) in three-necked flask continuously purged with gaseous N<sub>2</sub>, and the mixture of fiber/ionic liquid was stirred at 80°C up to 3 h to guarantee the complete functionalization of the fiber. To reduce viscosity and achieve suitable mixing, 5 mL DMSO was added to this mixture. The succinoylation reaction was carried out according to the following procedures.

To the fiber solution in ionic liquid/DMSO system, succinic anhydride (SA) and NBS, previously dissolved in 5 mL DMSO, was added at the corresponding reaction temperature with the 4:1 molar ratio of SA/AGU in fiber and the corresponding weight ratio of NBS/SA.

The mixture was heated in oil bath under N<sub>2</sub> atmosphere with magnetic stirring for the desired time. After the required time, the resulting mixture was slowly poured into 150 mL of isopropanol with stirring, washed thoroughly with isopropanol to eliminate ILs, unreacted anhydride, NBS, and byproducts, and then dried in a vacuum at 50°C for 16 h.

#### Silane treatment (Silanylation)

A solution of 5% v/v 3-aminopropyltriethoxy silane was prepared in acetone. Acetone was used in preference to water to promote hydrolysis to take place with the moisture on the surface of the fibers rather than within the carrier. The pH of

the solution was maintained at a value of 4 to bring about complete hydrolysis of the silane and to prevent self-condensation by the addition of acetic acid; the solution was stirred continuously for 10 min. Then, the fibers were added into the silane solution and kept mechanically stirring for 3 h at 35°C to ensure the adsorption of the silane onto the fibers. Afterwards, the fibers were rinsed with distilled water several times to remove chemical residues. Then, the fibers were dried for 3 days at ambient temperature and then oven-dried at 80°C (Seki *et al.*, 2018; Alan *et al.*, 2019).

#### Zinc chloride treatment

Zinc chloride treatment was done in accordance with the work done by Ejikeme *et al.* (2014) and Xiong *et al.* (2016). Anhydrous ZnCl<sub>2</sub> was added to a 250-mL beaker with an electric stirrer to obtain ZnCl<sub>2</sub> aqueous solutions with concentrations of 5%. The ZnCl<sub>2</sub> solution was mixed with Fibers (3%). Then, the system was stirred at temperatures of 50°C and time of 70 min. The regenerated cellulose was collected via filtration, followed by thorough washing with distilled water until the solution became chloride free and dried at 60°C for 24 h.

#### Characterization of modified sorbent

Characterization of the raw and modified sorbents was carried out through:

Fourier transform infrared (FTIR) analysis, Scanning electron microscope (SEM) analysis and Energy Dispersive X-ray(EDX) Analysis. This is to assess the functionalization and hydrophobicity of the modified sorbent.

#### FTIR spectroscopy: Fourier transformation infrared spectroscopy

Spectroscopy (FTIR) was recorded to identify a number of peaks and an organic functional group on the surface of the sorbent. The sample was mixed at a ratio of 1/100 and the wave numbers ranged from 4000 to 400 cm. A total of 20 scans were taken for each sample with 4 cm<sup>-1</sup> resolutions (Alan *et al.*, 2019; El din *et al.*, 2018).

#### Scanning electron microscope (SEM)

The morphology of the original and modified samples was monitored by a scanning electron microscope (Hitachi S-3000N) at an electron acceleration voltage of 30 kV. In order to prevent electron beam charging effect, the surfaces of the fibers were coated with a thin layer of gold to be more conductive before analysis (Shang *et al.*, 2016; Seki *et al.*, 2018).

#### Energy dispersive X-ray fluorescence (EDXRF) measurements

Determination of mineral composition available XRF equipment is portable AMPTEK(R) for Energy Dispersive X-ray Fluorescence (EDXRF) measurements. The original and modified fiber sample was placed on the sample holder of the XRF system and bombarded by X-ray fluorescence spectrometer with a Ag anode at a voltage of 25 kV and current of 50 mA. Sample need not to be coated. The equipment model is PX 2CR Power Supply and Amplifier for XR-100CR Si-pin Detector. Characteristic X-ray of the sample was detected by the solid state Si-Li detector system and spectrum acquisition was done using ADMCAR software. The spectrum analysis was done using the ADMCA plus Fundamental Parameter (FP-CROSS) software which translates the peak areas into concentration values (Nnaji *et al.*, 2016).

## Result and Discussion

### Extraction of fiber

Fiber was extracted from *Piliostigma reticulatum*. The sorbents were categorized into crude *Piliostigma reticulatum* (CPR), retted *Piliostigma reticulatum* (RPR), bleached *Piliostigma reticulatum*(PFPR) as shown in Fig. 1.



Fig. 1: *Piliostigma reticulatum* (crude, retted and bleached sorbents)

**Characterization of the crude oil sample (COS)**

The physicochemical Properties of Crude oil sample (COS) were determined. This includes the density, specific gravity, API gravity and viscosity. The results obtained are shown in Table 1.

**Table 1: Physicochemical properties of crude oil sample (COS)**

Properties	Values – Mean and Standard Deviation
Density (g/cm <sup>3</sup> )	0.8651 ± 0.01
Specific gravity (g/cm <sup>3</sup> )	0.8634 ± 0.01
API <sup>o</sup> gravity (30°C)	32.4 ± 0.02
Viscosity, 30°C (cSt)	5.04 ± 0.02

**Table 2: Physicochemical Properties of Sorbent**

Properties	CPR	RPR	PFPR
Moisture Contents (%)	12.69 ± 0.01	6.46 ± 0.02	3.89 ± 0.02
Ash Content (%)	11 ± 0.01	7.01 ± 0.01	9.02 ± 0.03
Volatile Content (%)	11.40 ± 0.02	61.33 ± 0.01	45.77 ± 0.02
Fixed Carbon Content	64.91 ± 0.01	25.15 ± 0.01	41.32 ± 0.01
Density (g/cm <sup>3</sup> )	1.0004 ± 0.03	1.0056 ± 0.01	1.0047 ± 0.01
Swell ability (%)	156.04 ± 0.02	200.56 ± 0.03	200.58 ± 0.02

**Characterization of the sorbent**

The results of the physical properties of the raw sorbents are presented in Table 2

**Sorption capacity studies**

The sorption capacity of the sorbent for remediation of crude oil polluted water were investigated and the results reported.

**Sorption studies for *Piliostigma reticulatum* (CPR, RPR, PFPR)**

The oil removal capacity of CPR, RPR and PFPR was reported. 0.3 g of the sorbent was used with contact of 20 minutes at initial oil concentration of 10 g/mL at temperature of 30°C. CPR sorbed 4.37 g/g, RPR 5.66 g/g and PFPR 5.24 g/g as seen from Fig. 2. This shows that RPR and PFPR has better sorption capacity than CPR. The higher oil affinity of

the RPR and PFPR compared to CPR can be attributed to pretreatment which disrupt the fibers primary walls and exposed the microfibrils causing improvement on the sorbent surface. The fact is that oil is easily adsorbed into the fiber assembly due to intermolecular interaction between the oil and the sorbent surface which has improved roughness due to pretreatment. Capillary action will also enhance the diffusion of oil through the successive fiber walls to the hollow lumen effectively in the pretreated sample (Rout *et al.*, 2016). The sorption capacity of the retted and bleached samples was higher than those of the crude sample (CPR) because the crude sample easily form dispersions in the water and latter settle at the base of the beaker after a while, making the sorption difficult.

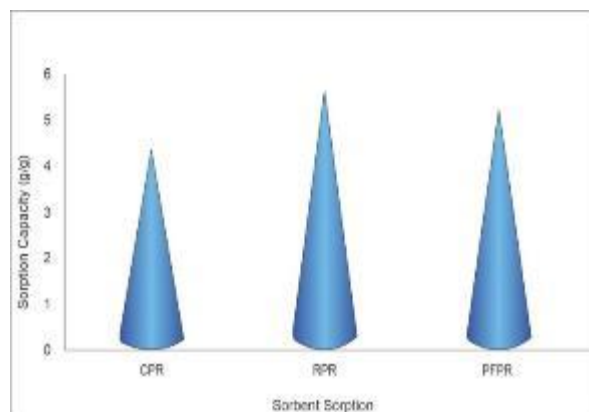


Fig. 2: Sorption capacity of CPR, RPR and PFPR

The crude *Piliostigma reticulatum* (CPR), retted *Piliostigma reticulatum* (RPR) and bleached *Piliostigma reticulatum* (PFPR) were subjected to sorption studies to optimize their sorption capacity. Factors that affect oil adsorption were investigated, namely the effect of variation in sorbent weight, contact time, oil concentration and temperature in water/oil medium. Tests were carried out at room temperature. The results revealed that the efficiency of sorbent to remove crude

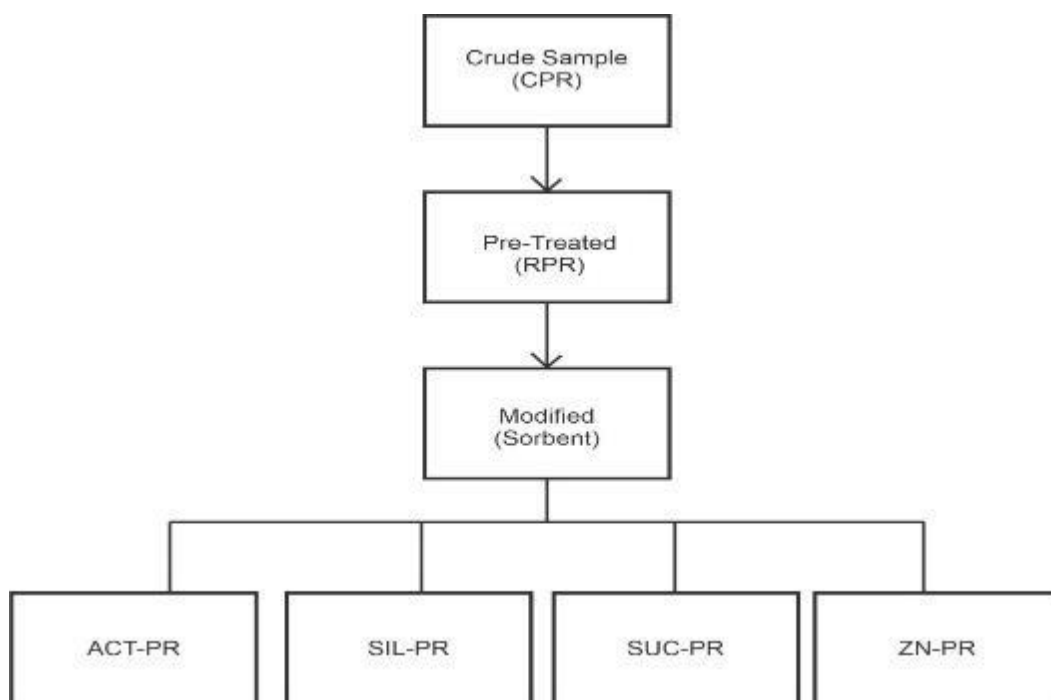
oil from water is related to the sorbent weight, contact time, initial oil concentration and temperature of sorption. It was found that increase in sorbent weight led to increase in sorption capacity from 4.22 - 5.20 g/g, 5.20- 7.92 g/g, and 4.70-6.75 g/g in CPR, RPR and PFPR, respectively. Increased in Initial oil concentration also increased the oil sorption capacity by 25-32%. Sorption time was varied from 10-70 min and the highest sorption capacity was recorded at 30 min. The effect of temperature was investigated from 30-60°C and increased in temperature causes decreased in sorption capacity with about 28-31%. The sorbent exhibited good reusability after 8 cycles, with less than 50% reduction in sorption capacity and RPR showed better retention capacity when compared with the other sorbent. This study will place *Piliostigma reticulatum* as a promising sorbent for crude oil remediation.

**Fiber surface treatment**

The sorbent (RPR) with the highest sorption capacity in this study was selected and modified. Four different chemical treatment were investigated: Acetylation, silanylation, Succinylation in Ionic liquid and addition of salt.

**Characterization of the selected sorbent**

The crude piliostigma reticulatum (CPR), selected retted piliostima reticulatum (RPR), acetylated sorbent (ACT-PR), silane treated sample (SIL-PR), succylated treated sample (SUC-PR) and Zinc chloride treated sample were all characterized to study the surface morphology before and after chemical treatment.



**Fig. 3: Process chart for characterization of selected sorbent**

**Fourier transforms infrared spectroscopy (FT-IR)**

FT-IR spectroscopy was employed to further characterize the chemical structures of the fibers. The structural changes in the fiber surface before and after treatment was investigated. The functional groups involved in oil sorption were identified via the determination of the chemical structure of the sorbents before and after oil sorption. Fig. 4 (A) shows the FTIR graph of crude (CPR), pretreated (RPR) sorbent and chemically treated sorbent samples (ACT-PR, SIL-PR, SUC-PR and ZN-PR). The IR spectra of untreated, pretreated and treated *Piliostigma reticulatum* fibers are depicted as shown from 4000 to 400 cm<sup>-1</sup> and Table 3 lists the position of peak with nature of bands of FTIR spectra. Therefore, it is expected that peak strength increases in some functional groups due to the increment in surface area and loss of certain functional group due to removal of certain lignocellulose part during chemical modification.

**Fourier transforms infrared spectroscopy of CPR**

A broad and strong band observed at 3467.2 - 3254.6 cm<sup>-1</sup> highlight the functional groups characteristic for cellulose referring to O-H stretching vibrations, due to hydrogen bonding in cellulose and lignin structure of the fiber. This vibration at 3467.2 cm<sup>-1</sup> is attributed to intramolecular hydrogen bonding. The intensive peaks at 2937 and 2853

cm<sup>-1</sup> are attributed to the asymmetric and symmetric stretching vibration of aliphatic CH<sub>2</sub> and CH<sub>3</sub> groups, indicating the presence of plant wax which is mainly composed of n-alkanes and a smaller portion of alcohols, fatty acids, aldehydes, ketones, and alkyl esters (Liu *et al.*, 2016; Narayanan *et al.*, 2018). The characteristic absorption peaks at 1749 and 1242 cm<sup>-1</sup> can be ascribed to the absorption of carbonyl stretching of esters and carboxyl groups, which are abundant in hemicelluloses. The band at 1635.3 cm<sup>-1</sup> relates to the bending mode of the absorbed water. The absorption peaks at 1595, 1504, 1462, and 1425 cm<sup>-1</sup> correspond to the stretching modes of C–O and C=C bonds in lignin. The strong absorption peak at 1047 cm<sup>-1</sup> is due to the C–O stretching in cellulose, hemicelluloses, and lignin or C–O–C stretching in cellulose and hemicelluloses. A small sharp band at 895 cm<sup>-1</sup> arises from the β-glucosidic linkages between the sugar units in hemicelluloses and celluloses. Table 3 shows the principal vibration modes as obtained from the spectra of Fig. 4 (A) together with their respective assignments to the fibers' components (Santos *et al.*, 2018).

**Fourier transforms infrared spectroscopy of RPR**

Based on the spectra presented in Fig. 4 (A) and Table 3, it can be suggested that NaOH gave rise to partial removal of hemicellulose and lignin. This can be proved by the

disappearance or loss of intensity of the main hemicellulose bands (1724  $\text{cm}^{-1}$ ) and lignin bands (1423, 1270, 1246 and 823  $\text{cm}^{-1}$ ). Due to the fact that the band at 1270  $\text{cm}^{-1}$  can be associated to both, cellulose (glucose rings) and lignin (guaiacyl rings), it does not disappear completely but loses intensity, which can be attributed to the solubilization of Lignin; cellulose is still present in the fiber structure after all alkaline treatments (Santos *et al.*, 2018). Fig. 4 (A) shows that the intensity of transmittance of the treated fibers is less than those untreated. This could be explained by the fact that the structure become less opaque after chemical treatment. This transparence could be attributed to the elimination of certain amount of lignin, hemicelluloses and other fatty and gammy substances.

The IR analyses clarified the elimination of hemicellulose by alkali treatment, which results in the untreated fiber bundle broken down into smaller ones (Zannen *et al.*, 2014). Compared to crude sample, the peak around 1730  $\text{cm}^{-1}$  (due to carboxylic and carbonyl groups from aldehydes, ketones as well as aromatic rings mainly from lignin part) is not observed in NaOH treated sample and shows intensity reduction for other chemical treatments due to lignin removal during the treatments. This is as a result of several reactions that take place during alkalization (Oushabi *et al.*, 2017; Ejikeme *et al.*, 2016). The intensity of the peak reduced after alkali treatment. In other words, the alcohol groups in cellulose structure get reduced with the alkali treatment (Sudha and Thilagavathi, 2015). This may be due to partial removal of the fattyacids which include hydroxyl groups that are involved in hydrogen bonding with the carboxyl group.

#### **Fourier transforms infrared spectroscopy of ACT-PR**

Compared with the aforementioned spectrums of pretreated sample, the spectrums of ACT-PR in Fig. 4 (A) provide definite evidences of acetylation. The spectrum of ACT-PR fiber exhibits obvious acetylation by three increased ester bands at 1750  $\text{cm}^{-1}$  (stretching vibration of the carbonyl group C=O in ester), 1374  $\text{cm}^{-1}$  (C-H bending vibration in -O(C=O)-CH<sub>3</sub>), and 1245  $\text{cm}^{-1}$  (C-O stretching vibration in ester (Mashkour *et al.*, 2015). In addition, the increments in the intensity of peaks at 2937 and 2853  $\text{cm}^{-1}$  in ACT-PR also indicate the process of acetylation. The obvious diminished peak intensity at 3440  $\text{cm}^{-1}$  indicates that a large percentage of hydroxyl groups are involved and replaced by acetyl groups. This explains the improvement of hydrophobic characteristic after the modification. Furthermore, the absence of absorption in the 1840– 1760  $\text{cm}^{-1}$  region proves the unreacted acetic anhydride has been thoroughly washed out with ethanol and acetone. The absorption band near 1700  $\text{cm}^{-1}$  for a carboxylic group cannot be found, which implies that the sample is also free of the acetic acid product generated in acetylation (Yang *et al.*, 2016).

#### **Fourier transforms infrared spectroscopy of SIL-PR**

Increase in the intensity of band after silane treatments may be due to the grafting of silane onto cellulose and the intermolecular condensation between adjacent adsorbed - Si-OH groups. The peaks observed between 2920 and 2700  $\text{cm}^{-1}$  were related to the C-H stretching vibration of alkyl groups in aliphatic bonds of cellulose, lignin and hemicelluloses (Orue *et al.*, 2015). After treatment procedures, the intensity of this peak slightly increased. The peak observed at 1239  $\text{cm}^{-1}$  indicating C-O stretching vibration of acetyl group in hemicelluloses showed diminishing intensity and further the peak 1734  $\text{cm}^{-1}$  corresponds to carbonyl groups related to hemicellulose disappeared after alkali treatment. The silane treatments caused further reduction of the band associated to lignin, probably due to the low pH of the silane solution (Rajkumar *et al.*, 2016; Erdogan *et al.*, 2016). The O-H bending of water absorbed into cellulose fiber structure was located at 1617  $\text{cm}^{-1}$ . The peak centered at 1507  $\text{cm}^{-1}$

corresponds to C-C in plane symmetrical stretching vibration of aromatic rings present in lignin. The small peak at 1157–1160  $\text{cm}^{-1}$  can be attributed to C-O-C asymmetric stretching (Sharma *et al.*, 2015). The absorption band at 1034  $\text{cm}^{-1}$  may be attributed to cyclic alcohol groups after alkali treatment, this band presented diminishing intensity whereas silane treatment increased this band noticeably.

#### **Fourier transforms infrared spectroscopy of SUC-PR**

Compared with spectrum 1 and 2, the spectra of succinylated sample provide evidence of succinoylation by the occurrence of the absorbance at 1732 and 1573  $\text{cm}^{-1}$ . Compared to the unmodified and pretreated samples, two new peaks at 1735 and 1568  $\text{cm}^{-1}$  were found in this modified sample. The overlapping band at 1732  $\text{cm}^{-1}$  is indicative of absorption by carbonyl group in carboxyl and esters. The band at 173  $\text{cm}^{-1}$  is assigned to the carbonyl groups in -COOH or -COOR, while the band at 1568  $\text{cm}^{-1}$  is characterized as the antisymmetric stretching of carboxylic anions indicating the formation of monoester providing the evidence of successful succinoylation (Liu *et al.*, 2016). In addition, the intensity of the absorption band at 1165  $\text{cm}^{-1}$  for C-O antisymmetric stretching increased after succinoylation, suggesting that the esterification reaction does occur. These significant changes of the absorption bands indicated that the monoester of succinylated cellulose was formed in ionic liquid/DMSO system under the conditions given. As expected, the absence of peaks at 1850 and 1780  $\text{cm}^{-1}$  in spectra for succinylated cellulose confirmed that the products are free of the unreacted SA (Xin *et al.*, 2017).

#### **Fourier transforms infrared spectroscopy of Zn-PR**

The reduction of the hydroxyl groups at 3404 and 1640  $\text{cm}^{-1}$  demonstrated the substitution of the hydroxyl groups. Fiber was recognized by the presence of large peaks at 1560 and 780  $\text{cm}^{-1}$ . Further these peaks were absent in the chemically treated fiber spectrum because of the removal of lignin by chemical treatments. The C-O-C symmetric glycosidic stretch at 1100  $\text{cm}^{-1}$  arose from the polysaccharide component that was largely cellulose and appeared for both untreated and treated fibers. It is observed that the treatment had changed the hydrophilic nature of the fibers into more hydrophobic nature. Amine group and C-H functional group from ZnCl<sub>2</sub>-treated sorbent show intensity reduction due to zinc and chloride ions reaction to these functional groups.

#### **Fourier transforms infrared spectroscopy of oil filled sorbent**

The FTIR spectra of the all the sorbents after sorption of crude oil are presented in Fig. 4(B). It can be concluded that there is no significant change in the spectral peaks of the sorbents before and after absorption of crude oil, except in the wave number 2922. 3  $\text{cm}^{-1}$  corresponding to -CH alkane stretching, common for all the sorbents, which can be attributed to addition of crude oil. The sorption of oil onto the surfaces of the sorbents was observed when the peak intensities at 2920 and 2852  $\text{cm}^{-1}$  increased after the oil sorption process (Cheu *et al.*, 2016). A well-pronounced peak at 1632  $\text{cm}^{-1}$  is associated with the presence of C=C stretching of aromatics for the oil adsorption. The adsorption of oil was further evidenced by the presence of a new peak at 1400  $\text{cm}^{-1}$  after the adsorption, which represents the C-H bending of oil (.Jahi *et al.*, 2015). The analysis of the IR spectra of the crude sorbent fiber showed characteristic features of lignin and hemicellulose components, which indicated that the fiber was lignocellulosic in nature. All above-mentioned results are in good agreement with the constituents of natural fibers including lignin, cellulose, hemicelluloses, and wax, which provide the original fibers a certain lipophilicity and precondition for further modification.

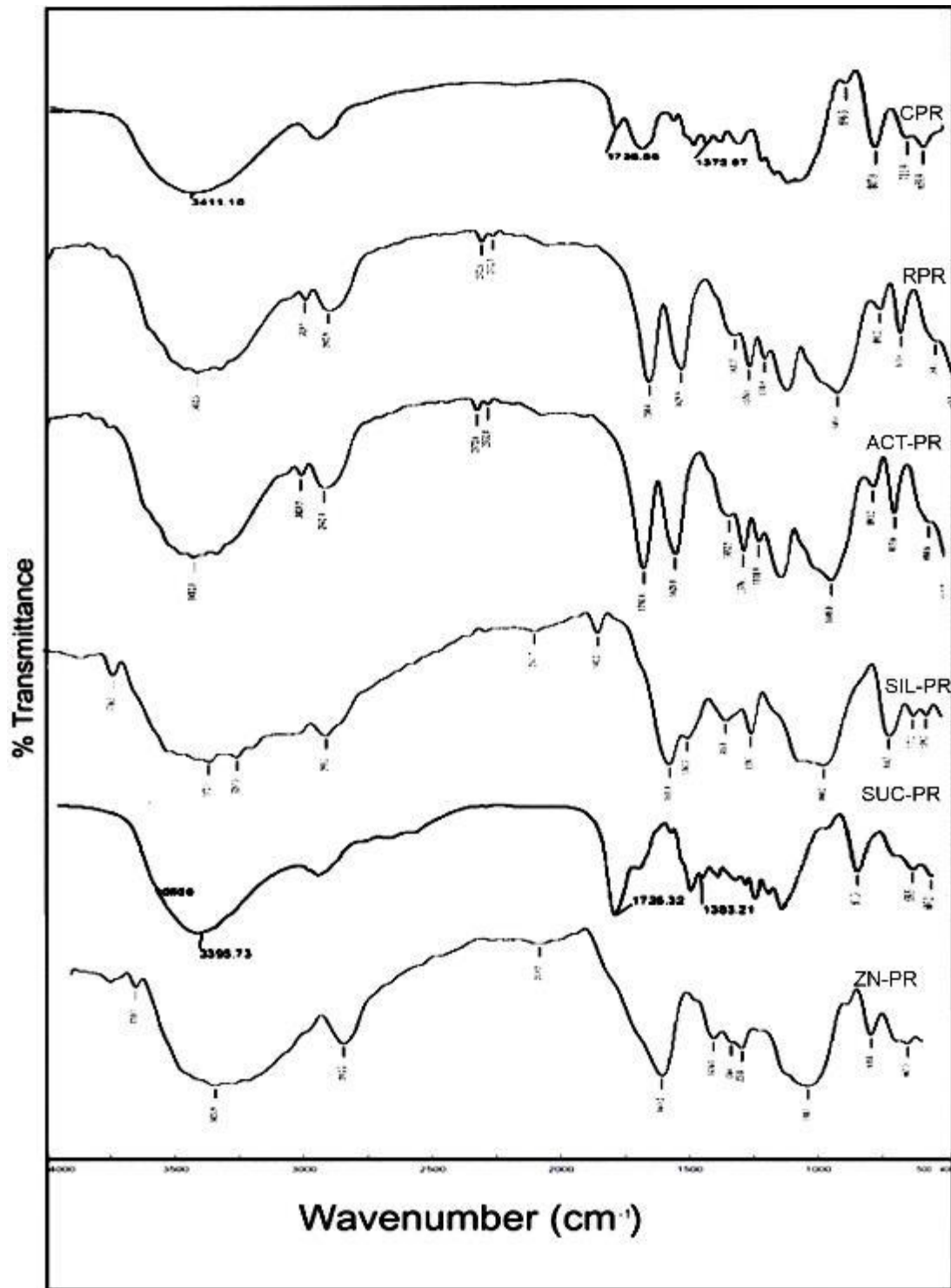


Fig. 4 (A): FT-IR spectra of CPR, RPR, ACT-PR, SIL-PR, SUC-PR and ZN-PR

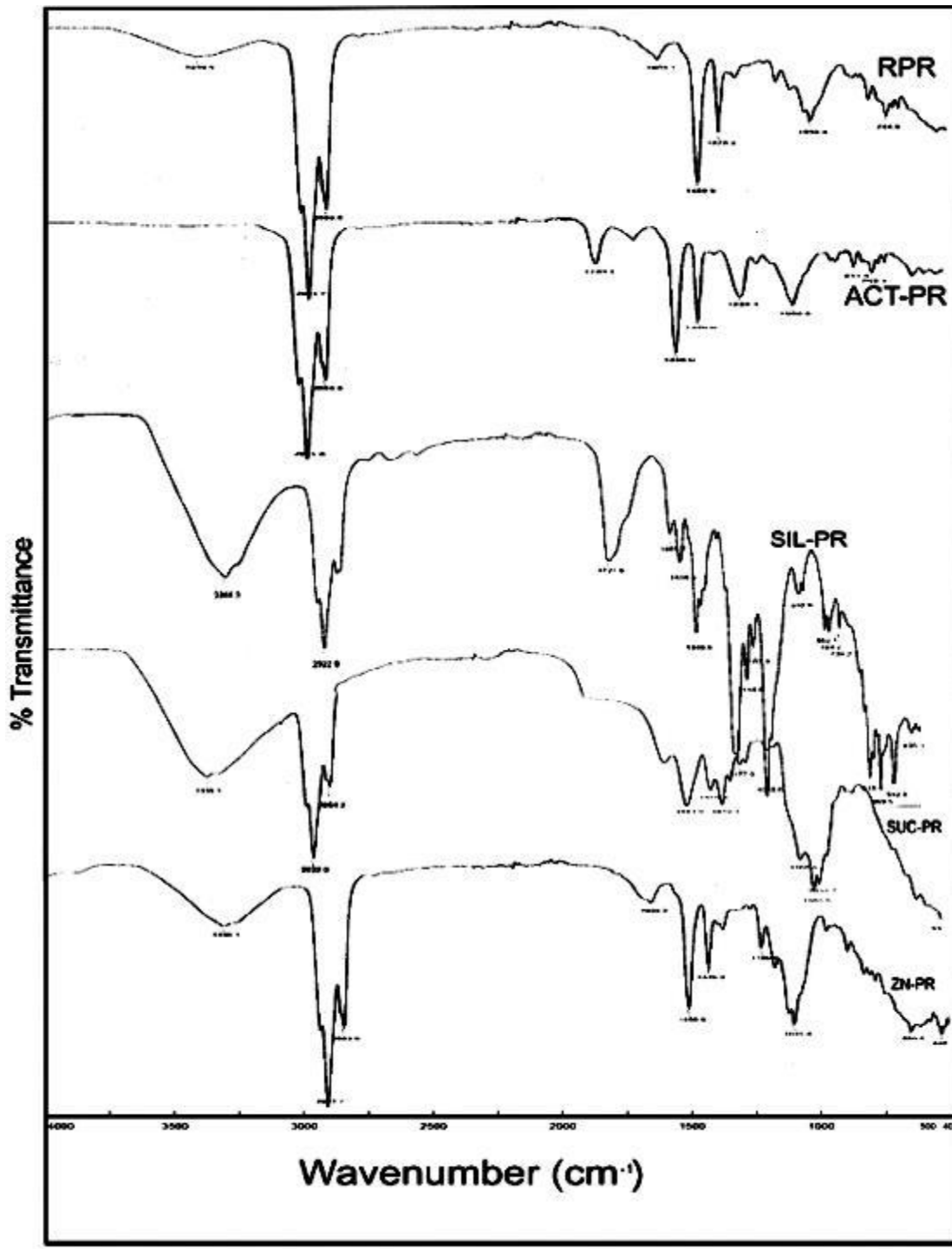


Fig. 4 (B): FT-IR spectra of oil filled CPR, RPR, ACT-PR, SIL-PR, SUC-PR and ZN-PR



Table 4.3: IR bands and their proposed associations to the infrared spectra of fiber components;  $\mu$ =stretching vibrations,  $\delta$ =deformation bands (Santos *et al.*, 2018)

IR region (cm <sup>-1</sup> )	Absorption peak (cm <sup>-1</sup> )	Peak attribution
3750-2800	3644	$\nu(\text{OH})$
	3340	$\nu(\text{OH})$
	2930	$\nu_s(\text{CH})_{\text{CH}_2}$
	2877	$\nu_s(\text{CH})_{\text{CH}_3}$
	1800-1500	1724
1500-1100	1610	$\nu(\text{C=C})$
	1513	$\nu(\text{CH})$
	1470	$\nu(\text{CO}_2)$
	1453	$\delta(\text{CH}_2), \nu(\text{C=C})$
	1423	$\nu(\text{O-CH}_2)$
1100-400	1375	$\delta(\text{CH})$
	1270	$\nu(\text{C-O-C})$
	1246	$\nu(\text{C-O})$
	1168	$\delta(\text{C-O-C})$
	1112	$\nu(\text{C-O})$
	1047	$\nu(\text{C-O})$
	898	$\beta$ -glycosidic bonding
	878	$\delta(\text{CO}_2)$
	823	$\nu(\text{C-H})$ aromatic

**Scanning electron microscopy (SEM)**

Scanning electron microscopy (SEM) provides an excellent technique for examination of surface morphology of fibers. SEM is the most common and simple device in studying the morphological properties of the solid samples. The SEM images of the crude *Piliostigma reticulatum* (CPR), retted *Piliostigma reticulatum* (RPR) after pretreatment with alkali and treated samples after modification through, Acetylation (ACT-PR), silanylation (SIL-PR), succinoylation in ionic liquid (SUC-PR) and salt treatment (Zn-PR) at different magnifications from 200, 50 and 20  $\mu\text{m}$  are shown in Figs. 5-10 (a, b, c).

SEM images of the sorbent samples from Figs. 5-10 (a, b, c) depicts a bundle-like structure which comprises of many elementary fibers (cells). The untreated fiber (CPR) Fig. 5 (a, b, c) present a compact surface with a lignin-cemented aspect and other vegetal tissues. As expected, the untreated fibers exhibit a smooth surface morphology compared to the treated ones as seen from the Micrograph. The SEM images show some wrinkles and roughness on the surface of the pretreated and modified sorbents. The percentage of wrinkles increased from one sample to another, depending on the treatment conditions (Taloub *et al.*, 2018).

The images clearly show major differences between untreated and treated samples. As indicated by the SEM image of CPR, noticeable impurities such as fats, oils and waxes can be observed. It is thought that modification influences both non-cellulosic (lignin and hemicellulose) and cellulosic (cellulose) components and surface impurities as well. Micro pores were not so apparent compared to the other samples. It was observed that NaOH pre-treatment had an impact on cleaning and removal of surface impurities as seen on Fig. 6 (a, b, c). It can be seen that it has fewer surface impurities when compared to Fig. 5, suggesting that it still contained a small

amount of native cellulose. This is probably due to the coverage by the large amount of regenerated cellulose (Xin *et al.*, 2017). It showed rough surface topography due to the removal of hemicelluloses, lignin, and amorphous waxy layer. Pretreatment promote surface defibrillation of the bundle, exposing elementary fibers due to the removal of hemicellulose and lignin. This increases the overall active surface area of the fibers, with more reactive sites for an effective chemical treatment (Alan *et al.*, 2019).

Micrograph resulting from the treated sample ACT-PR, SIL-PR, SUC-PR and Zn-PR, Fig. 7-10 (a, b, c) showed a cleaner surface in comparison to untreated one. However, surface particles are still visible at a lesser degree. This can be credited to a fact that none of the treatments (on their own) can impart desired qualities. A review made by Dong *et al.* (2015) found that treatment improved inter bonding strength of fibers in numerous ways like surface smoothness/roughness that encourages mechanical interlocking between fibers. The surface of the fiber becomes rougher and micropores were more visible compared to untreated fiber. The alkalization followed by acetylation, silanylation, succinoylation in ionic liquid and salt treatment changed the crude surfaces into corroded and coarse with high porous texture, the waxy layer of the crude fiber surfaces was removed, which increased the surface area for oil sorption. Chemical treatment resulted in more defined structures as more non-cellulosic materials and surface impurities were extracted. Figs. 7-10 showed a cleaner surface as more fats, waxes and surface impurities were removed. After treatment, the surface of sorbent became rough with many vertically arranged grooves. The roughing of the surface was favorable to oil sorption through fiber assembly, which significantly increased the available surface for oil absorption (Dong *et al.*, 2015).

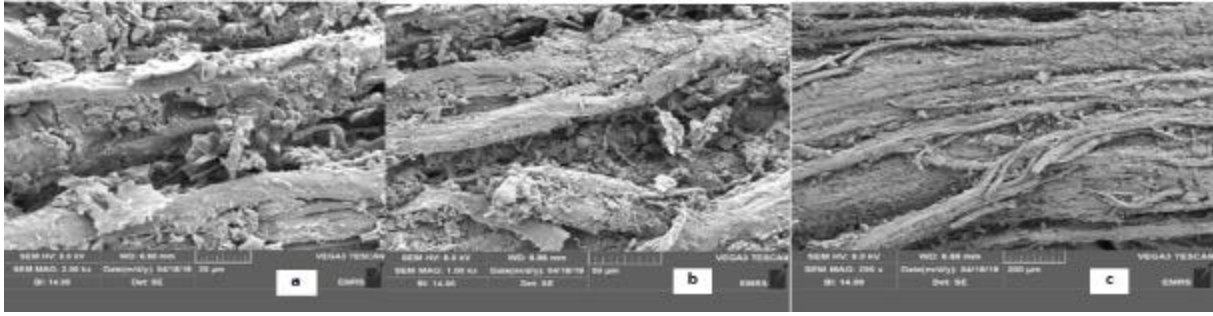


Fig. 5(a, b, c): SEM Images CPR (200, 50 and 20 um)

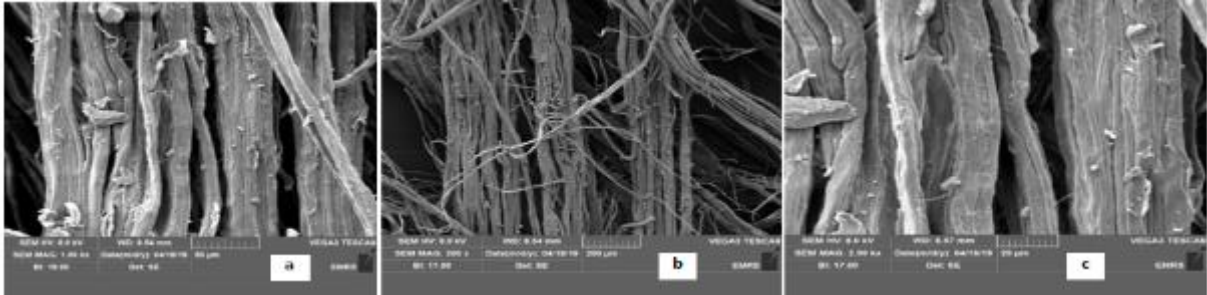


Fig. 6(a, b, c) : SEM Images RPR (200, 50 and 20 um)

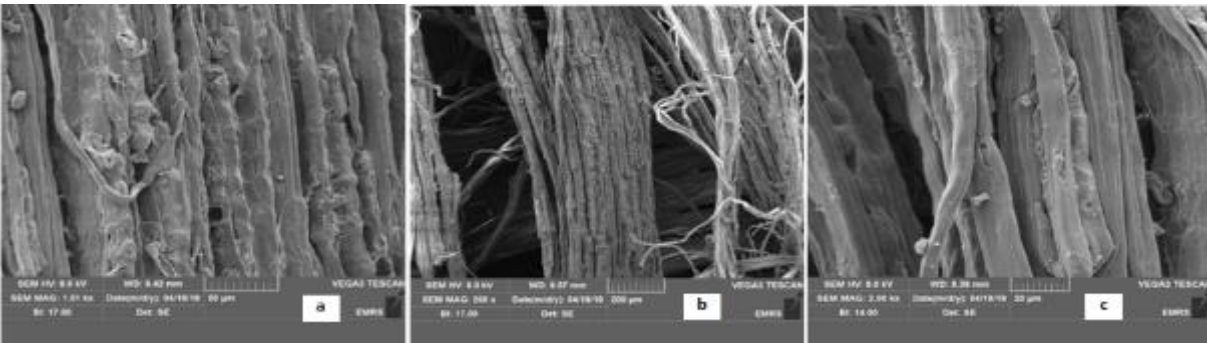


Fig. 7(a, b, c) : SEM Images ACT-PR (200, 50 and 20 um)

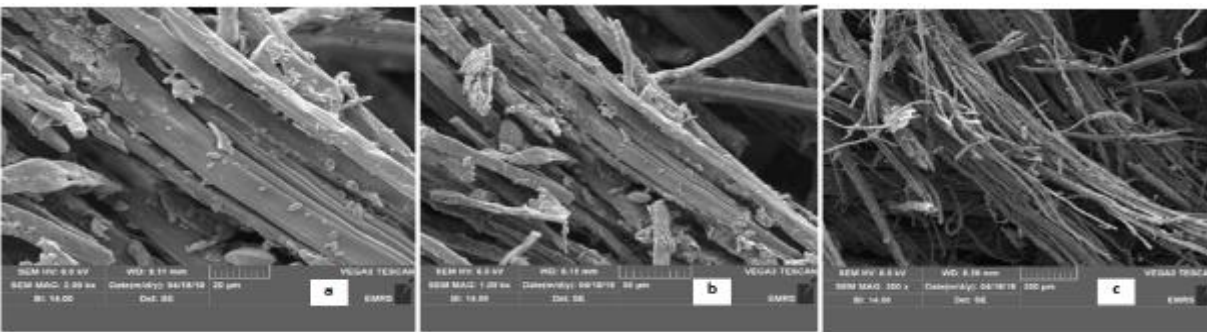


Fig. 8(a, b, c): SEM Images SUC-PR (200, 50 and 20 um)

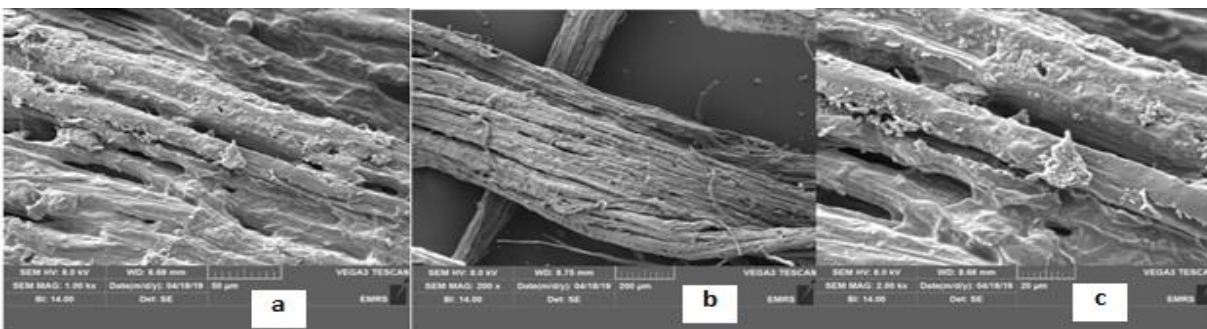


Fig. 9(a, b, c) : SEM Images SIL-PR (200, 50 and 20 um)

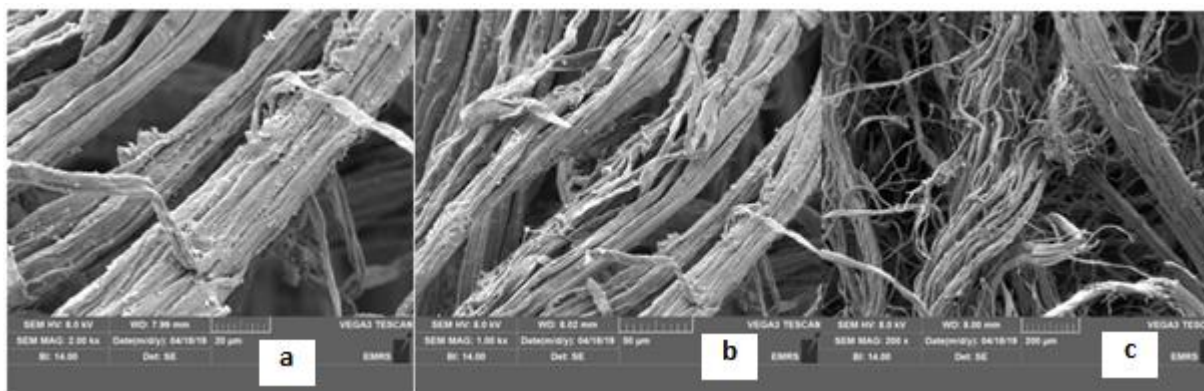


Fig. 10 (a, b, c): SEM Images ZN-PR (200, 50 and 20 um)

**Energy dispersive X-ray spectroscopy analysis (EDEX)**

Energy dispersive X-ray spectroscopy (EDX) is an excellent method to assess the quantity of elements that are distributed on the surface of the sorbents. EDX analysis offered weight and atomic percent of elements scattered on the surface of the sorbents. The elements existing in the sorbent are shown in the EDX micrograph in Figs. 11-16 (a, b). Carbon and oxygen are the major elements present in the EDX spectrum of all the sorbents which is the usual outcome of plant fiber. After pretreatment and modification most of the element appear only in smaller mass which were below 0.55%. EDX revealed that, the energy spectra of the x-rays character in the sorbent emitted from the crude sample, after pretreatment and treatment indicates that there is change in elemental composition in the samples after been subjected to the chemical modification. The result from EDX showed that the

concentration and distribution of elements were different prior to and after chemical treatment of the sorbents. High percentage of elements (C and O) showed in cluster, while other elements were in low percentage.

The elemental composition of the sorbent before treatment and after treatment by energy dispersive X-ray (coupled with SEM measurements) reveals a reduction in oxygen availability as evidenced by the decrease in peak height of oxygen signal. This accounts for the successful replacements of OH groups during acetylation, silylation, succinylation in ionic liquid, and addition of Zinc chloride. EDX results support results from infrared spectroscopy, in that, chemical treatment was effective due to efficient replacements of hydrophilic hydroxyl groups of cellulose by the hydrophobic groups which cover the fiber surface.

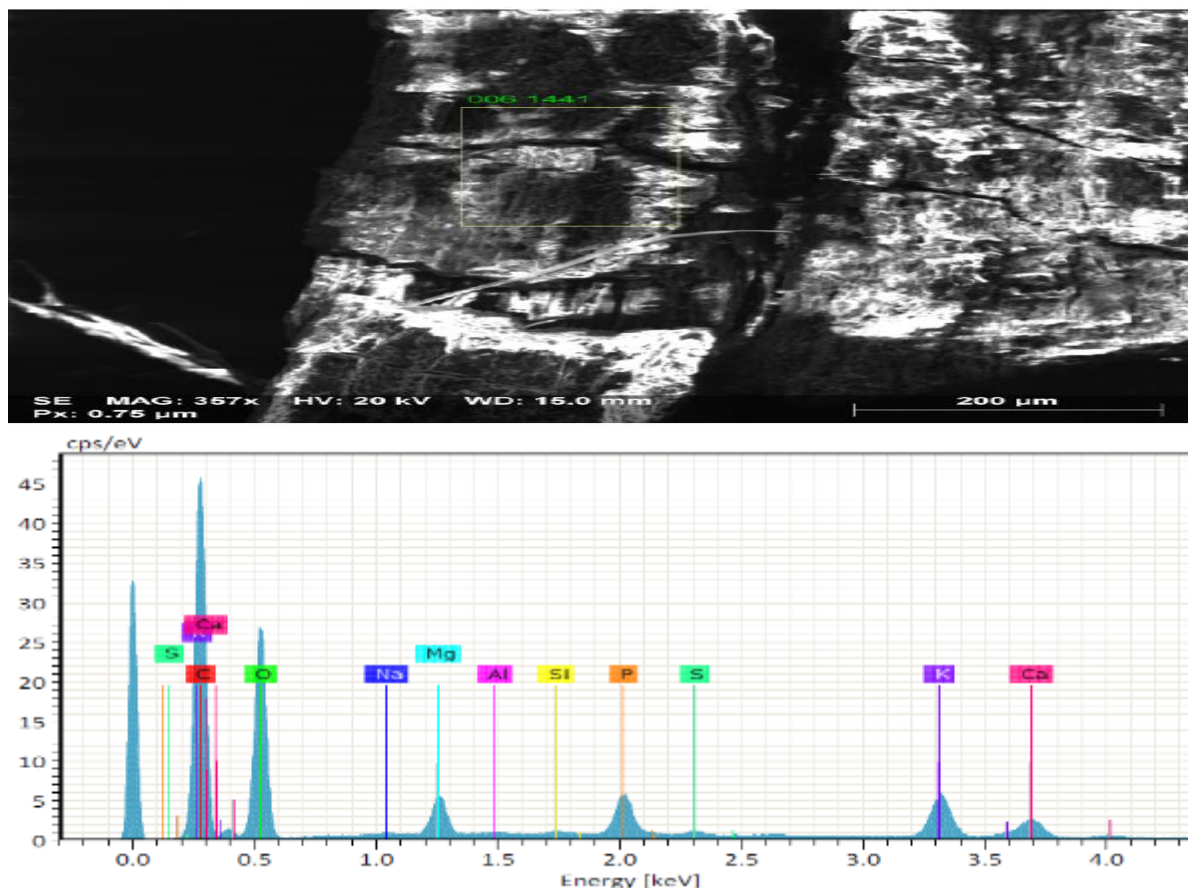


Fig. 11 (a): EDX spectrum (CPR)

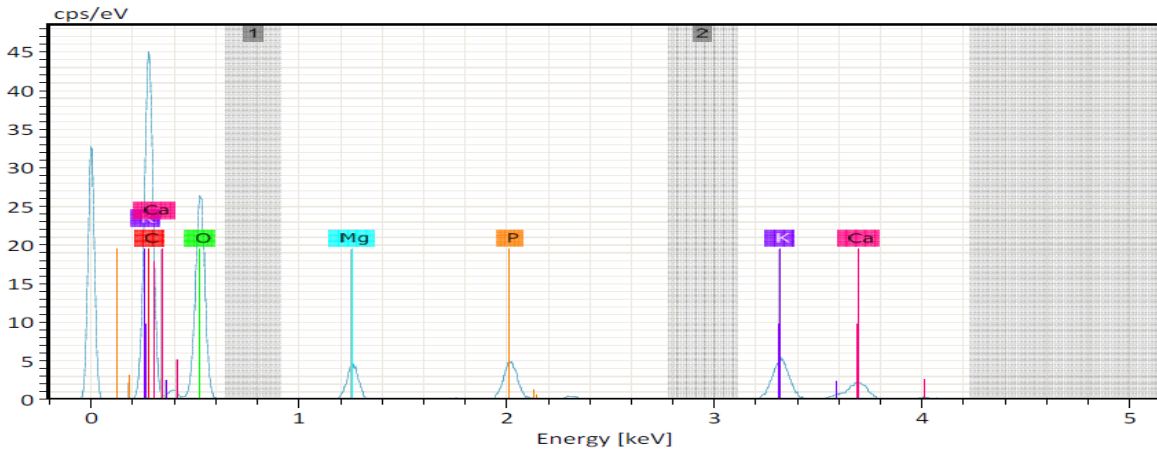


Fig. 11 (b): EDX spectrum (CPR)

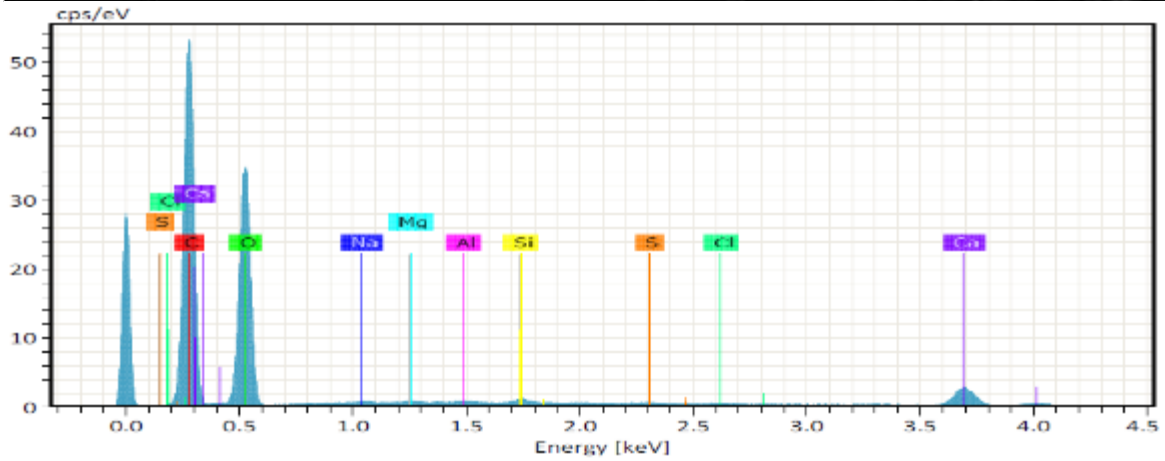
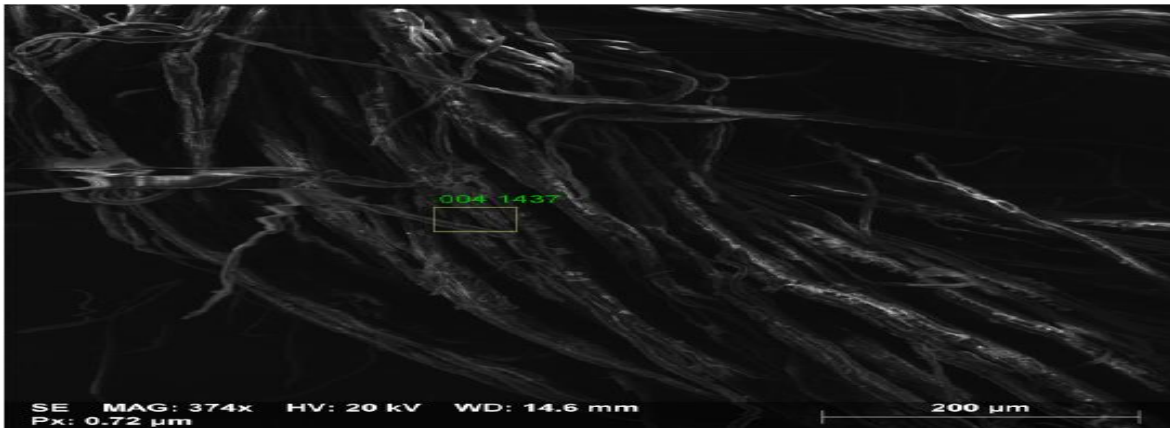


Fig. 12 (a): EDX spectrum (RPR)

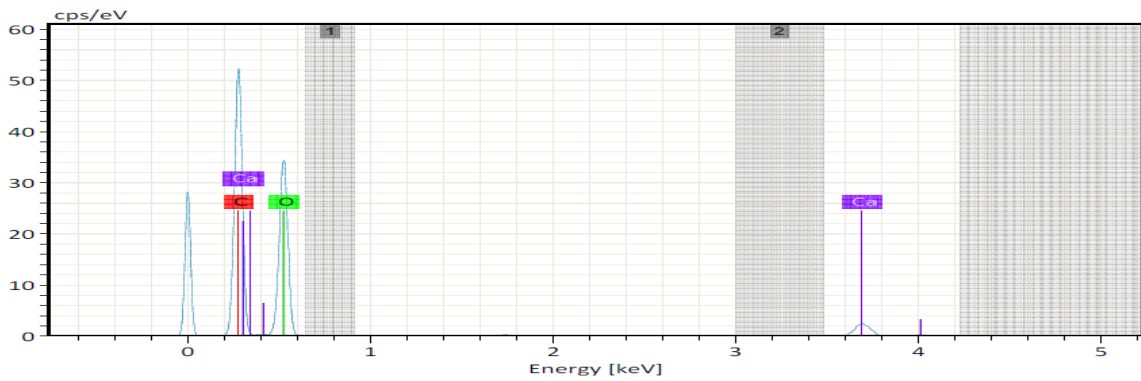


Fig. 12 (b): EDX spectrum (RPR)

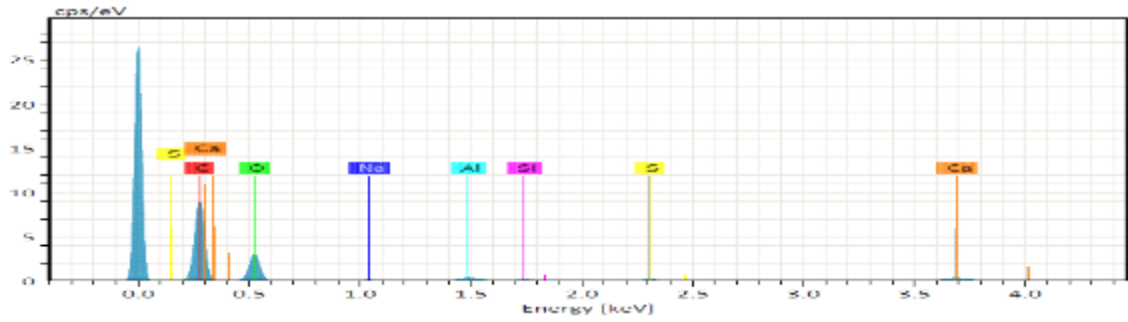
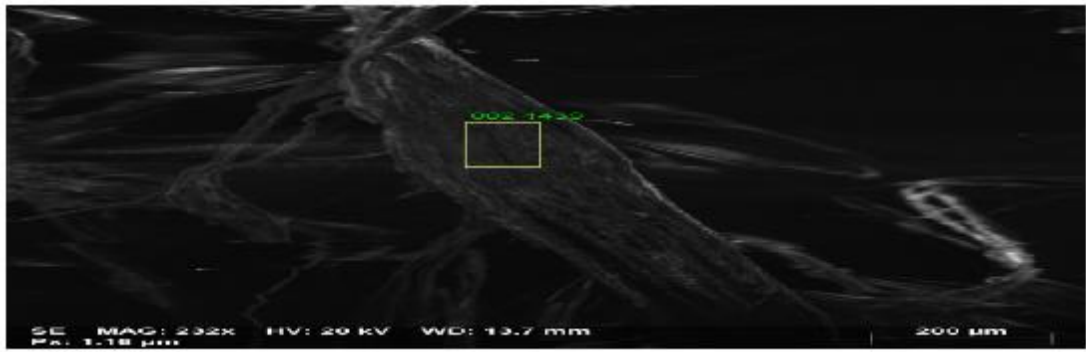


Fig. 13 (a): EDX spectrum (ACT-PR)

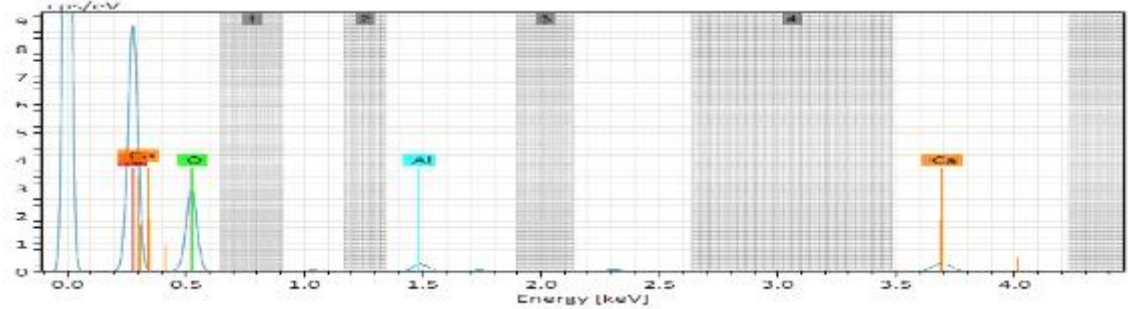


Fig. 13 (b): EDX spectrum (ACT-PR)

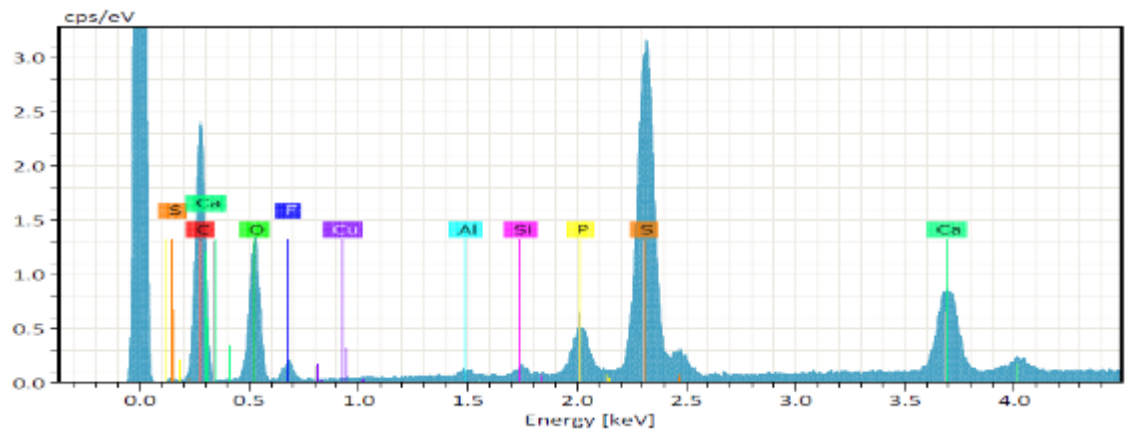
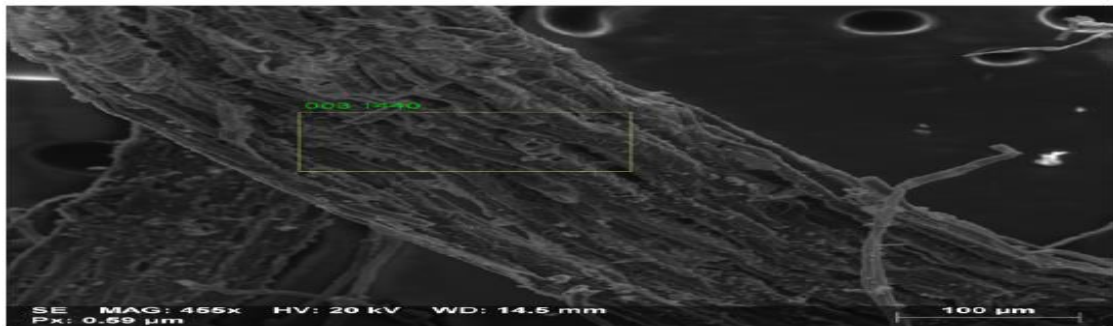


Fig. 14 (a): EDX spectrum (SUC-PR)

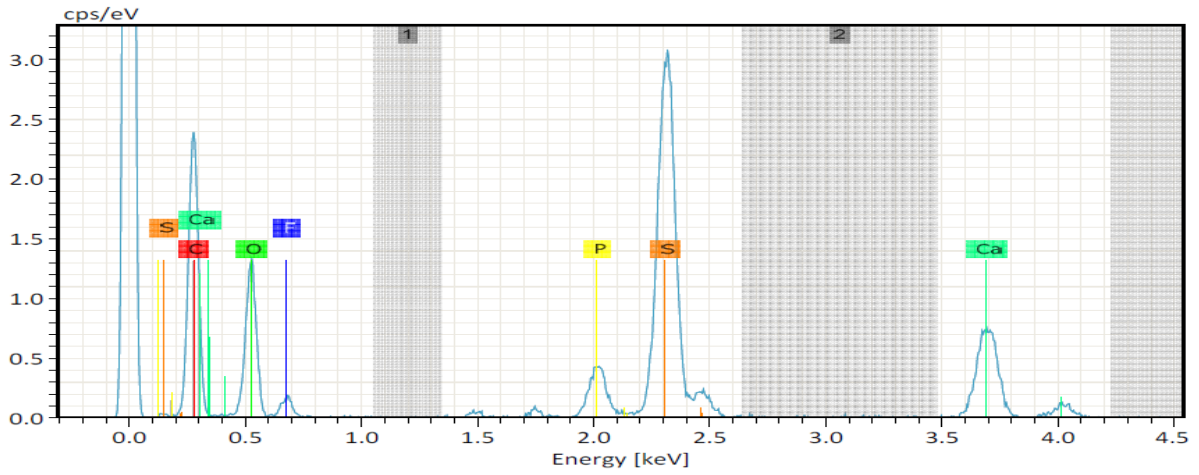


Fig. 14 (b): EDX spectrum (SUC-PR)

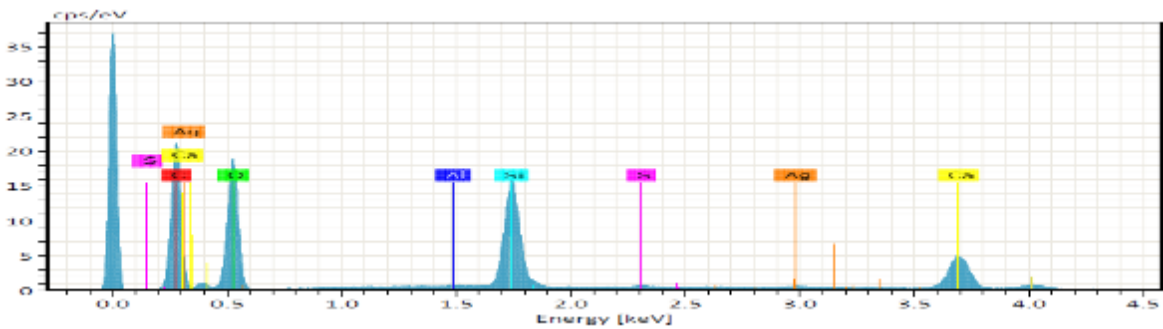


Fig. 15 (a): EDX spectrum (SIL-PR)

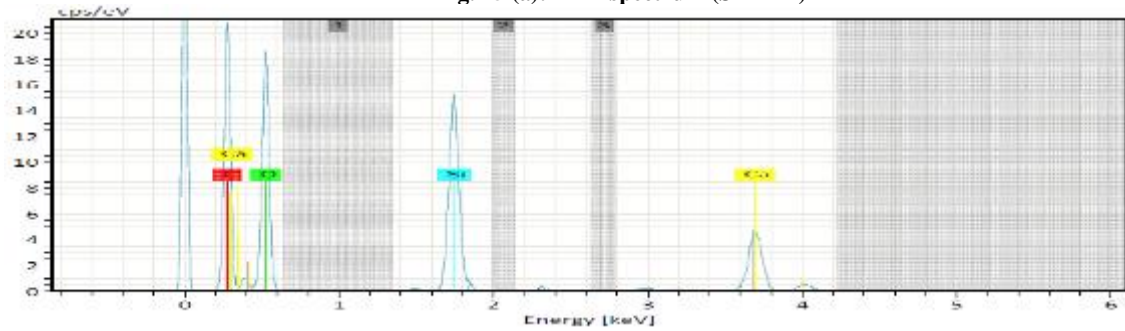


Fig. 15 (b): EDX spectrum (SIL-PR)

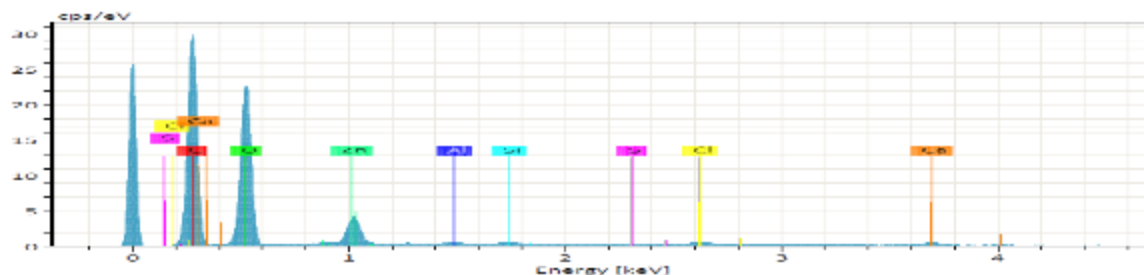
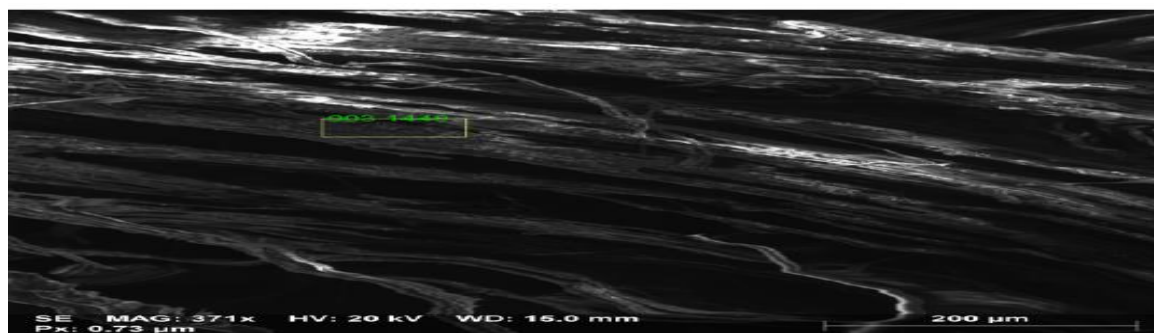


Fig. 16 (a): EDX spectrum (Zn-PR)

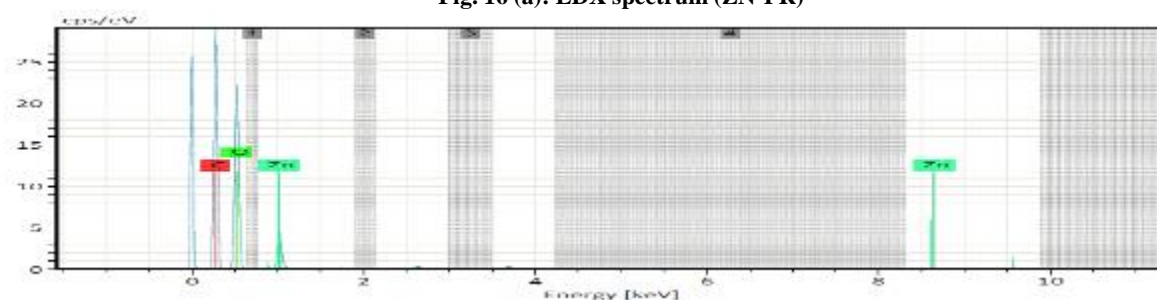


Fig. 16 (b): EDX spectrum (Zn-PR)

Table 4 showed the weight and atomic elemental composition percentage of the fiber captures by EDX. The emission of elements of carbon (C), oxygen (O), Magnesium (Mg), Phosphorus (P), Potassium (K), and calcium (Ca) were captured as dominant in the crude sample, RPR has (C, O, Ca) ACT-PR has (C, O, Al, Ca) SIL-PR has (C, O, Si, Ca) SUC-PR has (C, O, F, K, S, Ca) while ZN-PR has (C, O, Zn) at Mass greater than 0.05%.

SIL-PR	Carbon	40.35	52.02
	Oxygen	44.52	43.09
	Silicon	5.75	3.17
	Calcium	4.46	1.72
ZN-PR	Carbon	45.55	53.05
	Oxygen	53.46	46.74
	Zinc	0.98	0.21

Table 4: Surface atomic composition of the sorbent samples

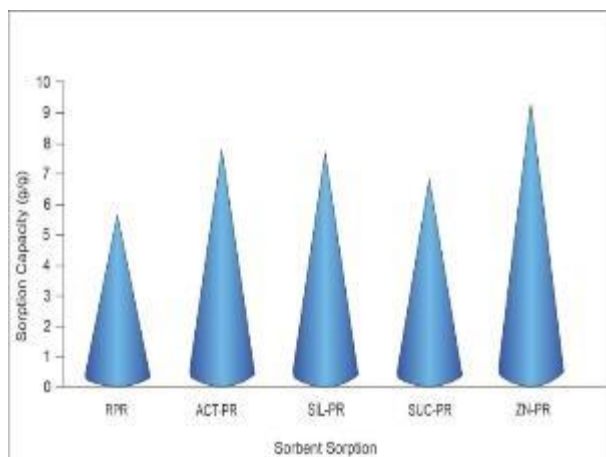
CPR	Element	Weight (%)	Atom (%)
CPR	Carbon	46.87	55.99
	Oxygen	45.73	41.02
	Magnesium	1.25	0.74
	Phosphorus	1.38	0.64
	Potassium	2.84	1.04
	Calcium	1.59	0.57
RPR	Carbon	46.55	54.08
	Oxygen	52.12	45.45
	Calcium	1.33	0.46
ACT-PR	Carbon	57.48	65.07
	Oxygen	40.33	34.27
	Aluminum	0.66	0.33
SUC-PR	Carbon	46.15	62.56
	Oxygen	26.62	27.06
	Fluorine	3.04	2.61
SUC-PR	Phosphorus	1.78	0.94
	Sulfur	11.49	5.83
	Calcium	2.40	0.97

*Sorption capacity studies of the selected and modified sorbent samples*

The sorption capacity of the selected and modified sorbent samples for remediation of crude oil polluted water were investigated and the results reported.

*Sorption studies of RPR, ACT-PR, SIL-PR, SUC-PR and ZN-PR*

The sorption capacity of the modified sorbent was compared to that of the pretreated sorbent RPR, to check the sorption capacity after chemical treatment. 0.3 g of the sorbent was used with contact of 20 min at initial oil concentration of 10 g/mL at temperature of 30°C. RPR has the least oil removal capacity of 5.69 g/g, compared to ACT-PR (7.79 g/g), SIL-PR (7.70 g/g), SUC-PR (6.84 g/g) and ZN-PR (9.31 g/g) as shown in figure 17. The reason for this observation can be attributed to the effects of surface modification on the physiochemical characteristics of the sorbent including surface functional groups, structure of the pores and surface area. The higher oil sorption capacity exhibited by the modified sample is an evidence of successful replacement of the water attracting hydroxyl group by hydrophobic group, increasing its potential to sorb more oil in an aqueous medium. This means that chemical modification can improved oil sorption.



**Fig. 17: Sorption capacity of RPR, ACT-PR, SIL-PR, SUC-PR and ZN-PR**

Optimization was carried out at different conditions. Factors that affect oil adsorption were investigated, namely the effect of variation in sorbent weight, contact time, oil concentration and temperature in water/oil medium. Tests were carried out at room temperature. The removal of crude oil increased steadily as the adsorbent mass was increased from 0.1 to 0.7 g in the pretreated sample while in the modified samples the optimum removal was at 0.5 g. Surface-modified sorbent (ACT-PR, SIL-PR, SUC-PR, Zn-PR) has noticeable high oil sorption capacity compared with the retted sample (RPR). RPR attained its highest sorption capacity of 7.92 g/g at 0.7 g of the sorbent weight, while ACT-PR, SIL-PR, SUC-PR, ZN-PR attained the highest sorption capacity of 10.51, 10.12, 8.52 g/g and 11.05 g/g at 0.5 g of the sorbent weight. This shows that a smaller adsorbent mass of modified sample is needed compared to the unmodified sample. Therefore, in the subsequent reactions, the sorbent dose was fixed at 0.5 g. Contact time of 10-70 min. was used for RPR and 5-35 min. for the modified samples. The effect of temperature was investigated from 30-60°C and increased in temperature causes decreased in sorption capacity. The sorbent exhibited good reusability after 8 cycles and RPR, ACT-PR, SIL-PR, SUC-PR and ZN-PR losses 33, 18, 17, 22 and 16%, respectively of the initial adsorb oil showing good retention capacity.

### Conclusion

Fiber was extracted from crude *Piliostigma reticulatum* (CPR), retted *Piliostigma reticulatum* (RPR), bleached *Piliostigma reticulatum* (PFPR). The physical properties of the sorbent and crude oil sample (COS) were determined. Sorption capacity studies were carried out. It was found out that variation in sorbent weight, contact time, initial oil concentration and temperature all affect the sorption capacity of the sorbent. RPR with the highest sorption capacity of 7.92 g/g at 0.7 g of the sorbent was selected for further modification. Modification of the selected sorbent was carried out by acetylation, succinylation in ionic liquid, silanylation and salt treatment. IR spectra of untreated, pretreated and treated sorbents showed peak strength increases in some functional groups due to the increment in surface area and loss of certain functional group due to removal of certain lignocellulose part during chemical modification. SEM images of the sorbent samples clearly show major differences between untreated and treated sorbent. EDX revealed that there is change in elemental composition in the samples after being subjected to the chemical modification. The sorption capacity of the modified sorbent was compared to that of the pretreated sorbent RPR, to check the sorption capacity after

chemical treatment. RPR has the least oil removal capacity compared to ACT-PR, SIL-PR, SUC-PR and ZN-PR. The reason for this observation can be attributed to the effects of surface modification on the physicochemical characteristics of the sorbent including surface functional groups, structure of the pores and surface area. The higher oil sorption capacity exhibited by the modified sample is an evidence of successful replacement of the water attracting hydroxyl group by hydrophobic group, increasing its potential to sorb more oil in an aqueous medium. This means that chemical modification can improve oil sorption.

### Conflict of Interest

Authors declare that there is no conflict of interest related to this work.

### Acknowledgement

Special appreciation to Simon Doherty research group, Newcastle University for the enabling environment, chemicals and instruments used to carry out this work.

### References

- Adeleye AS, Conway JR, Garner K, Huang Y, Su Y & Keller AA 2016. Engineered nanomaterials for water treatment and remediation: Costs, benefits, and applicability. *Chem. Eng. J.*, 286: 640-662.
- Alan MB, Sandra M, Irulapasamy S, Jebas TW & Sandro CA 2019. Effect of silane treatment on the Curaua fibre/polyester interface. *Plastics, Rubber and Compo.*, 48(4): 160-167 <https://doi.org/10.1080/14658011.2019.1586373>
- Almeida F, Meili L, Soletti J, Esquerre K, Ribeiro de Farias S 2019. Oil produced water treatment using sugarcane solid residue as biosorbent. *Revista Mexicana de Ingenieria Quimica*, 18” 27-33.
- Anjum M, Miandad R, Waqas M, Gehany F & Baraka AM 2016. *Arabian Journal of Chemistry*, pp 1-65. <http://dx.doi.org/10.1016/j.arabj.2016.10.004>
- Asadpour R, Sapari BN, Isa HM & Kakooei S 2016. Acetylation of oil palm empty fruit bunch fiber as an adsorbent for removal of crude oil. *Envt. Sci. Pollut.*, 23: 11740-11750 doi 10.1007/s11356-016-6349-2
- Boni H, de Oliveira D, Ulson de Souza A & Ulson de Souza S 2016. Bioadsorption by sugarcane bagasse for the reduction in oil and grease content in aqueous effluent. *Int. J. Environ. Sci. and Techn.*, 13(4): 1169-1176. DOI: 10.1007/s13762-016-0962-y
- Cai M, Takagi H, Nakagaito AN, Li Y & Waterhouse GN 2016. Effect of alkali treatment on interfacial bonding in abaca fiber-reinforced composites. *Compos A Appl Sci Manuf.* 90: 589-597. <https://doi.org/10.1016/j.compositesa.2016.08.025>
- Chen J, Xu J, Wang K, Cao X & Sun R 2016. Cellulose acetate fibers prepared from different raw materials with rapid synthesis method. *Carbohydrate Polymers*, 137: 685-692. DOI: 10.1016/j.carbpol.2015.11.034
- Donatus RB, Barminas JT & Riki EY 2016. Sorption studies of violet plant (*Securidaca longepedunculata*) root powder as sorbent in oil spill treatment. *Int. J. Scient. & Engr. Res.*, 7(4): 567-573. ISSN 2229-5518.
- Dong T, Xu G & Wang F 2015. Oil spill cleanup by structured natural sorbents made from cattails fibers. *Industrial Crops & Products*, 76: 25-33.
- Doshi B, Mika Sillanp M & Simo Kalliola S 2018. A review of bio-based materials for oil spill treatment. *Water Research*, 135: 262-277.
- Ejikeme PCN, Ejikeme EM & Nwosu DC 2014. Effect of chemical treatments on *Mpelocissus cavicaulis* fiber. *Int. J. Applic. or Innov. in Engr. & Mgt.*, 3(11): 96-104.



- Ejikeme PCN, Ejikeme EM & Chime TO 2016. Optimization of chemical treatment of *Morinda morindoides* fiber. *J. Multidisc. Eng. Sci. & Tech.*, 3(10): 5651- 5660.
- El-din AG, Amer BG & Malsh H 2018. Study on the use of banana peels for oil spill removal. *Alexandria Engineering Journal*, 57: 2061–2068.
- El-Gendy NS & Hussein NN 2016. Study on the effectiveness of spent waste sugarcane bagasse for adsorption of different petroleum hydrocarbons water pollutants: kinetic and equilibrium isotherm. *Desalin. Water Treat.*, 57(12): 5514-5528.
- Golam T, Mohammad NI, Seong-Jae P & Jeong-Hun P 2018. Optimization of operating parameters to remove and recover crude oil from contaminated soil using subcritical water extraction process. *Envntal. Engr. Res.*, 23(2): 175-180.
- Hubbe AM 2013. Review of cellulosic biosorption. *Lignocellulose*, 2(2): 386-411.
- Khalid J, Soleiman H & Al-Sayah HM 2018. Preparation of oil sorbents by solvent-free grafting of cellulose cotton fibers. *Cellulose*, 25(7): 4093–4106.
- Liu J, Li Peng, Chm Li, Feng Y, He W, Yan X & Lu X 2016. Superhydrophilic and underwater superoleophobic modified chitosan-coated mesh for oil/water separation. *Surf. Coating. Technol.*, 307: 171-176.
- Lv W, Xia MT & Yuewu P 2017. Preparation of an efficient oil-spill adsorbent based on wheat straw Ermeng. *Bio Resources*, 12(1): 296-315.
- Muhammad IM, El-Nafaty UA, Surajudeen A & Makarfi YI 2015. Oil removal from produced water using surfactant modified Eggshell. *Energy and Biotechnology*, 85: 84-92
- Narayana C, Upadhyay RK, Chaturvedi R & Sagar R 2017. A versatile carbohydratebased gelator for oil water separation, nanoparticle synthesis and dye removal. *New J. Chem.*, 41: 2261.
- Nnaji NN, Onuegbub UT, Edokweb O, Ezech CE & Ngwud PA 2016. An approach for the reuse of *Dacryodes edulis* leaf: Characterization, acetylation and crude oil sorption studies. *J. Envntal. Chem. Engr.*, 4: 3205–3216.
- Nwabueze HO, Igbokwe PK, Amalu EU & Okoro SE 2015. A study on the equilibrium and kinetics of oil spill cleanup using acetylated corn cobs. *Int. J. Envntal. Sci.*, 5(6): 0976 – 4402.
- Nwadiogbua OJ, Ajiweb EV & Okoyeba AC 2016. Removal of crude oil from aqueous medium by sorption on hydrophobic corncobs: Equilibrium and kinetic studies. *Journal of Taibah University for Science*, 10: 56–63.
- Onwuka CJ, Agbaji BE, Ajibola OV & Okibe GF 2018. Treatment of crude oil-contaminated water with chemically modified natural fiber. *Appl. Water Sci.*, 8: 86 <https://doi.org/10.1007/s13201-018-0727-5>
- Onwuka JC, Agbaji EB, Ajibola VO & Okibe FG 2016. Kinetic studies of surface modification of lignocellulosic *Delonix regia* pods as sorbent for crude oil spill in water. *J. Appl. Res. Techn.*, 14: 415–424.
- Oushabi A, Sair S, Oudrhiri HF, Abboud YO, Tanane O & El Bouar A 2017. The effect of alkali treatment on mechanical, morphological and thermal properties of date palm fibers (DPFs): Study of the interface of DPFePolyurethane composite. *South Afri. J. Chem. Engr.*, 23: 116-123.
- Paulauskiene T & Jucike I 2015. Aquatic oil spill cleanup using natural sorbents. *Environ. Sci. Pollut. Res.*, 22: 14874-14881.
- Rahman SN, Yhaya FM, Azahari B & Ismail RW 2018. Utilisation of natural cellulose fibers in wastewater treatment. *Cellulose*, 25: 4887–4903.
- Santos BE, Morenoa GC, Barrosa PJ, Araújo de Mouraa D, Fima CF, Riesc A, Wellena RR & Balbino da Silvaa L 2018. Effect of alkaline and hot water treatments on the structure and morphology of piassava fibers. *Materials Research*, 21(2): e20170365. DOI: <http://dx.doi.org/10.1590/1980-5373-MR-2017-0365>
- Seki Y, Ahmet C, Kilinc A, Dalmis R, Atagur M, Serhan K, Ali AG, Erdal C, Mehmet O & Ali B 2018. Surface modification of new cellulose fiber extracted from *Conium maculatum* plant: a comparative study. *Cellulose*, 25: 3267–3280 <https://doi.org/10.1007/s10570-018-1797-0>
- Shang W, Sheng Z, Shen Y, Ai B, Zheng L, Yang J & Xu Z 2016. Study on oil absorbency of succinic anhydride modified banana cellulose in ionic liquid. *Carbohydr. Polym.*, 141: 135–142.
- Wang J, Geng G, Wang A, Liu X, Du J, Zou Z, Zhang S & Han F 2015. Double biomimetic fabrication of robustly superhydrophobic cotton fiber and its application in oil spill cleanup. *Industrial Crops and Products*, 77: 36-43. DOI: 10.1016/j.indcrop.2015.08.044
- WHO 2015. Drinking-water: World Health Organization (WHO) Fact sheet N° 391. <http://www.who.int/mediacentre/factsheets/fs391/en/>
- Wolok E, Jamal Barafi J, Navneet Joshi N, Rossella Girimonte R & Sudip Chakraborty 2020. Study of biomaterials for removal of the oil spill. *Arabian Journal of Geosciences*, 13(1244): 1-11.
- Xin P, Huang Y, Hse C, Cheng HN, Huang C & Pan H 2017. Modification of cellulose with succinic anhydride in TBAA/DMSO mixed solvent under catalyst-free conditions. *Materials*, 10: 526; doi:10.3390/ma10050526
- Xiong J, Yu S, Zhu H, Wang S, Chen Y & Liu S 2016. Dissolution and structure change of bagasse cellulose in Zinc chloride solution. *Bioresources*, 11(2): 3813-3824.
- Xu Y, Su Q, Shen H & Xu G 2019. Physicochemical and sorption characteristics of poplar seed fiber as a natural oil sorbent. *Textile Research Journal*, 0(00): 1–9. DOI: 10.1177/0040517519829001
- Younis SA, El-Gendy NS, Waleed IEA & Moustaf YM 2014. Kinetic, isotherm, and thermodynamic studies of polycyclic aromatic hydrocarbons biosorption from petroleum refinery wastewater using spent waste biomass. *Desalin. Water Treat.*, 56(11): 3013-3023.
- Zamparas M, Tzivras D, Dracopoulos V & Ioannides T 2020. Application of sorbents for oil spill cleanup focusing on natural-based modified materials: A review. *Molecules*, 25(4522): 1-22.
- Zannen S, Ghali L, Halimi TM & Hassen BM 2014. Effect of chemical extraction on physicochemical and mechanical properties of Doum palm fibres. *Advances in Materials Physics and Chemistry* 4(10): 203-216.
- Zou J, Chai W, Liu X, Li B, Zhang X & Yin T 2015. Magnetic pomelo peel as a new absorption material for oil-polluted water. *Desalination and Water Treatment* 57(27): 12536-12545. DOI: 10.1080/19443994.2015.1049958.