Original Research Article

POTENTIAL USE OF *HIBISCUS ASPER* (RAMAN KOGI) FIBRE AS OIL SORBENT

ABSTRACT

The effect of acetylation on *Hibiscus asper* fibre using acetic anhydride has been investigated. The acetylation was carried out in a free solvent system under mild conditions using acetic anhydride, in the presence of calcium chloride as a catalyst, at a temperature of 100^oC for 3 hour. The crude oil and the *Hibiscus asper* sorbent were characterized, the sorption behaviors studied were found to increase with increase in weight per gain percent (WPG%). The WPG% and oil sorption capacity indicated the success of acetylation. Fourier transform infrared spectroscopy (FT-IR) was used for the analysis of unmodified and modified *Hibiscus asper* sorbent to further examine the success of acetylation. In the spectra of FT-IR of the acetylated *Hibiscus asper* material evidence of acetylation is clearly proven by, the enhancement of 1755 cm^{-1}, as 1755.31-1715.97 cm^{-1} which are carbonyl C=O stretching of esters, the enhancement of 1494.97 -1403.35 cm^{-1} of (C-H bond in $–O(C=O)-CH_3$ and the appearance of 1154.69- 1154.43 cm^{-1} which is a C=O stretching of acetyl group. The values for correlation coefficient (R^2) showed that the model fitted the Langmuir isotherm (R^2 *Hibiscus asper* 0.99) better than the Freundlich isotherm, indicating that the adsorption process was monolayer. The higher oil sorption capacity shown by the modified *Hibiscus asper* sorbent compared to the lower oil sorption capacity of unmodified, indicated that the modified *Hibiscus asper* sorbent can substitute for synthetic fibres and recommended for oils spill clean-up in contaminated environments.

Key words: Adsorption, oil spill, sorbents, *Hibiscus asper,* fibre, Langmuir isotherm.

INTRODUCTION

World's source of energy is fuel and is been transported by ships across ocean and by pipelines across land, hence a number of spills occurred. Also the production of petroleum products increased from 50 million tons in mid 1950s to 2,500 million tons by the mid-1990s, these result in the massive transportation and associated oil spills (Nwilo and Badeje, 2007). Oil spills are common occurrences today because of the many uses of oil in the society. Oil spills from vessels or land based facilities can pose serious threats to shorelines, banks and other sensitive habitats. In Nigeria oil spill is a common event (Baird, 2002) and occur due to a number of causes, including corrosion of pipelines and tankers (accounting for 50% of all spills), Sabotage (28%) Oil production operators (21%) inadequate or non-functional production equipment (1%) (Nwilo and Badeje, 2001).

It is known that commercially available synthetic sorbent are very costly due to the facts that a lot had been spent in the production unlike the natural plant sorbents which are abundantly available and cheap. Agricultural waste sorbent is abundantly available around the world and several different methods of development with or without catalyst have been developed. A number of natural sorbents have been modified and studied for use on oil cleanup, for example; cotton (Johnson *et al*., 1973; Choi *et al*., 1993, Choi, 1996), wool (Radetic *et al*., 2003), bark (Haussard *et al.,* 2003), barley straw (Hussein *et al.*, 2008), Kenef (Lee *et al*., 1999) and corn-cobs (Diya'udeen *et al*., 2008). They were observed to be excellent oil sorbents because of their hydrophobic and oleophilc character.

Chemical modification of plant or wood materials to improve their dimensional stability has been the subject of research for many years. A wide variety of chemicals have been studied including anhydrides, acid chlorides, carboxylic acids isocyanates, acetals, esters, acetyl chloride, B-propiolactone, acrylonitrile and exposides. Cellulose sorbents have been chemically treated (Sun *et al*., 2004) and research into the use of their modified products as absorbents for the removal of crude oil from aqueous solutions have been on the increase. A lot of research is being carried out to develop natural plants materials for oil spill cleanup. Modified natural plants have shown very high capacity to sorbs oil from sites, Rice Husks (Nwankwera, et al, 2011), Barley Straw (Husseine, et al, 2008).

The English name of the plant is River hemp or water hemp, the plant belongs to the family *Malvaccae* and the botanical name is *Hibiscus asper*, the Hausa name is Ramar-raafii or Ramar ruwa but the common name is Hibiscus asper . The Fulani people called it follere (plural pole) Roger Blench and Mallam Dendo (2006). It grows along the river bank, the bark is used as ropes and the leaves is used as a vegetable in some West African delicacy soup.

The aim of this research work is to investigate the possibility of using *Imperata cylindrical* fibre as a sorbent for oil spill clean-up due to fact its abundantly availability and cheap.

MATERIALS AND METHODS

Sample Collection and Preparation

The plant sample *Hibiscus asper* (Figure 1), was collected from a farm land located in Girei Local Government Area, Adamawa State, Nigeria and identified by a Botanist from Modibbo Adama University of Technology, Yola .

The sample obtained was cut from the stem with a knife, the bark was removed washed with distilled water and was spread on a clean polyethene and allowed to dry in the laboratory for one week. It was crushed using piston and mortar and then sieved using improvise mesh and left to dried at 65^{o}C in the oven which was stored in a labeled polyethene bags. The crude oil sample was collected in a sample bottle from Port-Harcourt Refinery in River State, Nigeria.

Figure 1: Picture of *Hibiscus asper* (Raman Kogi) plant at sample location

Extraction Procedure

5g of the bark sample was extracted with the mixture of ethanol-toulene (2:1 v/v) for 3hours. After extraction the samples was rinsed with ethanol followed by hot water and oven dried at 105^{o}C for 24 hours to reach a constant weight. The extractible content was calculated as a percentage of oven dried test samples.

Chemical Modification

The acetylation was carried out in mild conditions in the presence of calcium chloride using acetic anhydride by Sun *el al* (2004) in a free solvent system. 5g of sample was placed in a 500ml flat bottom flask containing 300cm^3 of the acetic anhydride and 30g of calcium chloride. The flask was placed into a thermostatic water bath set at 100^{o}C under atmospheric pressure, with a reflux condenser fitted, the flask was removed from the water bath and the hot reagent was decanted off. The sample material was thoroughly washed with ethanol and acetone to removed unreacted acetic acid by-product. The new product was oven dried at 60^{o}C for 8 hours. The dried modified *Hibiscus asper* fibre was re-weighed to determine the weight gain on the basis of initial oven dry measurement, weight percent gain % (WPG) of the *Hibiscus asper* fibre due to acetylation was calculated from the formula:

$$WPG\ (\%) = [\ (W_{mod} - W_{unmod}) / W_{unmod}] \times 100$$

Where W_{mod} is the oven dried weight of the modified *Hibiscus asper* and W_{unmod} is the weight of the *Hibiscus asper* prior to reaction.

Characterization of the sorbents

Moisture content

The moisture content was determined according to the method of Rengaraj *et al.,* (2000).

Ash content

Ash content was determined using the methods employed by Aloko & Adebayo (2007).

Volatile Content

The Volatile content was determined according to the method of Fapetu (2000).

Fixed carbon

The fixed carbon was determined as adopted by Fapetu (2000)

Bulk density

The method described by Ekpete and Horsfall (2011) was adopted.

Porosity

This was determined by the method adopted by Ekpete and Horsfall (2011).

Specific gravity

This was determined by the method adopted by Ekpete and Horsfall (2011.

Swellability (S) and Anti- swelling efficiency (ASE) tests

The swellabilty and anti-swelling activities were determined as adopted by Termiz (2006)

Characterization of Crude Oil Sample

The following physico-chemical properties were used to characterize the crude oil sample from Port-Harcourt.

Density

The density of the crude oil was determined using a specific gravity bottle as adopted by Nwankwere (2011).

Viscosity

The viscosity of the crude oil was obtained using a viscometer at 25^oC

Specific gravity

The specific gravity (s.g) of the crude oil was calculated using the result obtained for density. The specific gravity being a more standard measurement was obtained by multiplying the density obtained with the density of water 0.998g/dm3

The American Petroleum Institute (API)

This was obtained using the method describe by Nwankwere (2011)

Crude oil sample weathering

The crude oil contains low boiling fractions that evaporates after a spill and is often before significant cleanup operations can take place. Therefore in order to simulate the situation of the oil spill and to minimize experimental variation, the crude oil samples was placed in beakers for one day in an open air to released volatile hydrocarbons contents.

Oil sorption studies

Oil sample 20ml was suspended in 150ml of water in a 250ml beaker, different weights of the plant material was spread on the surface of the mixture, the procedure was repeated at room temperature, after 20 minutes the plant material was collected with a net and left to drained by hanging the net suspended by retort and clamp over the beaker for 15 minutes. The entire procedure was carried out at various conditions to test the effect of sorbent weight, reusability and time of acetylation. The oil sorption capacity was calculated from the formula:

Sorption capacity =new weight gain/ original weight x100

Determination of the amount of water sorption

The water content of the sorbent was determined in the laboratory using the method of centrifuge technique as carried out by Hussein *et al* (2008). The plant material was subjected to pressing to desorb the crude oil. During the pressing stage petroleum ether (10-20ml) was added to help extracted the oil in the sorbent, the extracted liquid was collected in a centrifuge tube. The centrifuge tube was put in a water bath to break emulsion present and then centrifuge for 20 minutes. The amount of water sorbed was weighed and recorded.

Fourier Transform Infrared Spectroscopy Analysis (FT-IR)

The modified and unmodified properties of *Hibiscus asper* samples were characterized using FT-IR, Perkin-ELMER-8000S Spectrophotometer. Samples were run using the KBr pellet technique at the National Research Institute for Chemical Technology (NARICT), Zaria, Kaduna-Nigeria.

Statistical data analysis

The data obtained was analyzed using the method for calculating mean and standard deviation expressed as estimate standard deviation S of a finite set of experimental data (N< 30) at 95% confidence level and two degrees of freedom.

$$S = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{N - 1}}$$

RESULTS AND DISCUSSIONS

The results of the physical properties of the unmodified and modified plant materials shown that during the course of the modification the ash contents which is the reflection of the inorganic composition is within the range of the general ash content (1%-20%) of the fibrous raw material. After modification Hibiscus asper has the ash content of 13%, moisture content reduced by 11%, hence the plant materials will have low water intake and become more hydrophobic. The swellability was decreased from 680% - 407%, making the plant materials a better sorbent for oil retention as swellability influences competition between oil and water for sorption sites in the sorbent. The oil sorption capacity also increases from 320% - 449%, this shows that the acetylation of the plant materials makes it a possible sorbent for oil spill application Nwankere et al. (2010). The improvement and changes in the physical properties of the plant materials after acetylation is an indication of a successful acetylation, the WPG of Hibiscus asper was 224%.

The results of the physical properties of the unmodified and modified plant materials were reported as seen in the Table 1.

Table 1 Characterization properties of *Hibiscus asper*

Characterizing properties	unmodified	modified
Ash Content (%)	6.00±0.01	13.00±0.01
Moisture content (%)	4.00±0.01	11.00±0.03
Volatile content (%)	98.00±0.05	50.00±0.01
Bulk Density (g/cm^3)	1.24±0.01	1.14±0.01
Fixed Carbon (%)	-4.00± 0.01	37.00±0.01
Specific Gravity (g/cm^3)	0.017±0.01	0.018±0.01
Sweallability (Absorption)	608±0.01	407±0.02
Oil Sorption Capacity (%)	320±0.01	449±0.02

The properties of the crude oil characterized were the density, specific density, API gravity, viscosity and the ash content. The results obtained are shown in Table 2.

The results of the characterized oil show its lightness in the recorded density of less than 1 and specific gravity which makes a promising sorbent, the viscosity at 30^{o}C is 3.06 mpa.s, these properties tend to affect the way oil samples are being absorbed by the sorbents.

Table 2. Characterization of the crude oil sample

Parameters	Values
Density (g/cm^3)	0.91±0.01
Specific gravity (g/cm^3)	0.85±0.02
*API (30^{O}C)	35.07±0.01
Viscosity (30^{O}C, mpa.s)	3.06±0.01
Ash content (%) @ 700^{O}C	11.80±0.01

*API – American Petroleum Institute, PHCO-Port-Harcourt crude oils

In this research the weight per gain (WPG) increased as the temperature increases which are an indication of effective Acetylation. The relationship between the temperature of acetylation of Hibiscus asper and the weight per gain is illustrated in Table 3. This result agreed with the work done by Nwankwere (2010), where acetylated rice husk showed increased in weight per gain with increased temperature during modification.

Table 3. Effect of Temperature and time on the natural plant sorbents

	Temperature (^{0}C)				
	10^{o}C	20^{o}C	30^{o}C	40^{o}C	60^{o}C
Time (min)	WPG (%)				
10	1.7	2.0	2.3	2.5	2.7
20	1.9	2.1	2.5	2.7	2.9
30	2.0	2.4	2.7	3.0	3.6
40	2.4	2.6	3.0	3.2	3.9
50	2.8	2.9	3.2	3.5	4.1
60	3.0	3.3	3.5	3.9	4.5
80	2.7	2.9	3.0	3.6	3.9
100	2.5	2.7	2.8	3.4	3.7
120	2.2	2.5	2.1	3.2	3.5

The oil/water sorption ability of the natural plant materials was examined in order to understand the sorption capacity of the sorbents Table 4. There was an increase in sorption capacity for oil/water with increase in sorbent weight for the natural plant materials. The modified plant materials showed higher sorption capacity than the unmodified. The oil/water sorption by unmodified *Hibiscus asper* increased from 10.62g/g to 34.20g/g,

Table 4. Oil and water sorbed by unmodified and modified *Hibiscus asper*

Weight Of Sorbent (g)	Sorption time (mins)	Oil and water sorbed (Unmodified) (g/g)	Oil and water sorbed (Modified) (g/g)
0.5	60	10.62	14.4
1.0	60	16.26	18.06
1.5	60	18.78	21.96
2.0	60	27.24	31.68
2.5	60	34.20	36.42

The oil sorption capacity recorded by the natural plant materials as shown in Table 5. The unmodified oil sorption of *Hibiscus asper* was 13.14g/g and it increased to 24.09g/g. The higher oil sorption capacity shown by modified plant materials is an evidence of successful replacement of the water attracting hydroxyl group by acetic anhydride, thus chemical modification has improved water absorption due to acetylation.

Table 5. Oil sorbed by unmodified and modified *Hibiscus asper*

Weight of Sorbent (g/)	Sorption time (mins)	oil sorbed unmodified (g/g)	oil sorbed modified (g/g)
0.5	60	13.14	18.96
1.0	60	17.88	23.82
1.5	60	19.29	25.32
2.0	60	22.02	28.23
2.5	60	24.09	31.08

Water sorption capacity of *Hibiscus asper* was examined to understand the water sorption ability of the sorbent (Table 6). The unmodified plant materials showed higher water uptake at 60 minutes compared to water uptake by the modified.

Water uptake by unmodified *Hibiscus asper* was 6.33g/g and it increased to 18.39g/g. Modification was achieved by acetylation which resulted in less water uptake by the modified plant materials.

Table 6. water uptake capacity by unmodified and modified *Hibiscus asper*

Weight of Sorbent (g)	Sorption time (mins)	water uptake unmodified (g/g)	water uptake modified (g/g)
0.5	60	6.33	3.33
1.0	60	9.06	6.99
1.5	60	12.99	10.02
2.0	60	16.23	13.59
2.5	60	18.39	16.03

The effect of reusability of *Hibiscus asper* was carried on crude oil as shown in Tab OS (MOD) (g/g) showed that the acetylated *Hibiscus asper* was reused three times before it reached 50% of the original sorption capacity. This could be due to the irreversible deformation of the natural plant materials as a result of tearing, crushing and other deterioration during squeezing. It's evident that the acetylated sorbents could be efficient in recycling as seen practically in its stable floatability with much cycles carried out.

Table 7. Effect of 1g acetylated reusability of *Hibiscus asper*

Weight of sorbent (g)	No. of Cycles	Sorption time(min)	Oil sorbed (g/g)
1	1	60	11.25
1	2	60	11.70
1	3	60	12.60
1	4	60	12.30
1	5	60	12.00

The results of the acetylation of the natural plant materials using different concentrations of acetic anhydride and catalyst are shown in Table 8. The solid to liquid ratio of Hibiscus asper observed at 1.20 and 1.60 of sorbent to acetic anhydride mixture resulted to the increased of WPG from 3.67± 0.01to 7.61±0.01 respectively. The structural modification by introducing the acetyl groups in place of the hydrogen of the hydroxyl group is evident with increased in the WPG. The catalyst (Calcium Chloride) dosage from1-3% have shown efficient Acetylation and the use of catalyst in Acetylation does not only speed the rate of hydroxyl group bond breaking by chlorinating mediated analysis, but also its an advantage of removing hemicelluloses components of the organic material, which is highly responsible for the sorbent hydrophilicity is significant. This work unfolded a new modified fibre product that could have sorbent oleophilicity needed for cleaning of an environment contaminated.

Table 8. Effect of acetic anhydride and catalyst on *Hibiscus asper*

Solid/liquid	Temperature (^{0}C)	Reaction time (1hours)	Catalyst (%)	WPG(%)
1.20	60	1	1.0	3.67
1.30	60	1	1.5	4.81
1.40	60	1	2.0	5.77
1.50	60	1	2.5	6.05
1.60	60	1	3.0	7.61

The sorption studies obtained for the sorbents in water, oil and both oil and water indicated increased sorption with increased weight of the sorbent as reported similarly by Hussein, *et al.,* (2008), there was low water pick up by the modified natural plant materials as compared to the unmodified samples.

The effect of WPG on oil absorptivity of the sorbent showed that because of the small hydroxyl groups are substituted with larger acetyl groups, the sorbent will remain in a permanently swollen state and thus become heavier. A higher WPG showed a higher degree of Acetylation, because the acetyl groups added are responsible for increased oil sorption by the acetylated sorbent, therefore it is expected that the WPG increases, the sorption capacity of the sorbent would increase simultaneously. Sorption qualities of barley strands , both revealed increased time with increased sorption time. Table 9 showed that the oil sorbed by *Hibiscus asper* increased from 4.12g/g to 5.90g/g,

Table 9. Effect of sorption time on 1g of *Hibiscus asper*

WOS (g)	Time (min)	Oil Sorbed (g/g)
1	20	4.12
1	30	4.93
1	40	5.11
1	50	5.54
1	60	5.9

Correlation coefficient (R^2) is an important indicator to determine which isotherm fit the system and the highest (R^2) will fit the system The Freundlich value for *Hibiscus asper* was k = 2.52, n = 1.28 and R^2 was 0.27. For Langmuir value a = 0.02, b = 0.02 and R^2 = 0.99. These results (Table 12) showed that acetylated plant materials fitted Langmuir model isotherm for it has the highest R^2 value the adsorption can be described as monolayer. The values of R^2 for the plant material sorbents indicated that it is an excellent sorbents to clean-up oil spilled in a contaminated area.

Table 10. Langmiur isotherm of *Hibiscus asper*

Ce/Qe	**Ce**
0.03	0.5
0.04	1.0
0.06	1.5
0.07	2.0
0.08	2.5

Table 11. Freundlich isotherm of *Hibiscus asper*

Log Ce	**log Qe**
- 0.03	1.28
1.00	1.38
0.18	1.40

0.30	1.45
0.40	1.50

Table 12: Langmuir and Freundlich isotherms model constant

	Langmuir model			Freundlich model		
	a	b	R^2	k	n	R^2
Hibiscus asper	0.02	0.02	0.99	2.52	1.28	0.27

The characteristics of a particular functional group in a molecule in general are shown by the vibrational frequencies. A distinct O-H stretching in the region of 3390.62 cm^{-1} to 3175.99 cm^{-1} and C-H stretching in methyl and methylene groups (2923.23 cm^{-1}) and absorptions in the region from 1030.22cm^{-1} to 1755.31cm^{-1} (Owen and Thomas, 1989) are characteristics of these plant materials. Structural units that undergo various changes are the functional groups located on the glucose monomer in the cellulose as observed in the FTIR spectra (Bodirlau and Teaca, 2009). The peaks observed at 418.88, 418.25, 721.48 and 1031.22 cm^{-1} are associated with the unmodified plant materials while those absorbed at 3755.78, 3353.64, 3673.61 and 3626.76 cm^{-1} in the spectra of the acetylated plant materials provided some evidence of Acetylation in the modified plant materials.

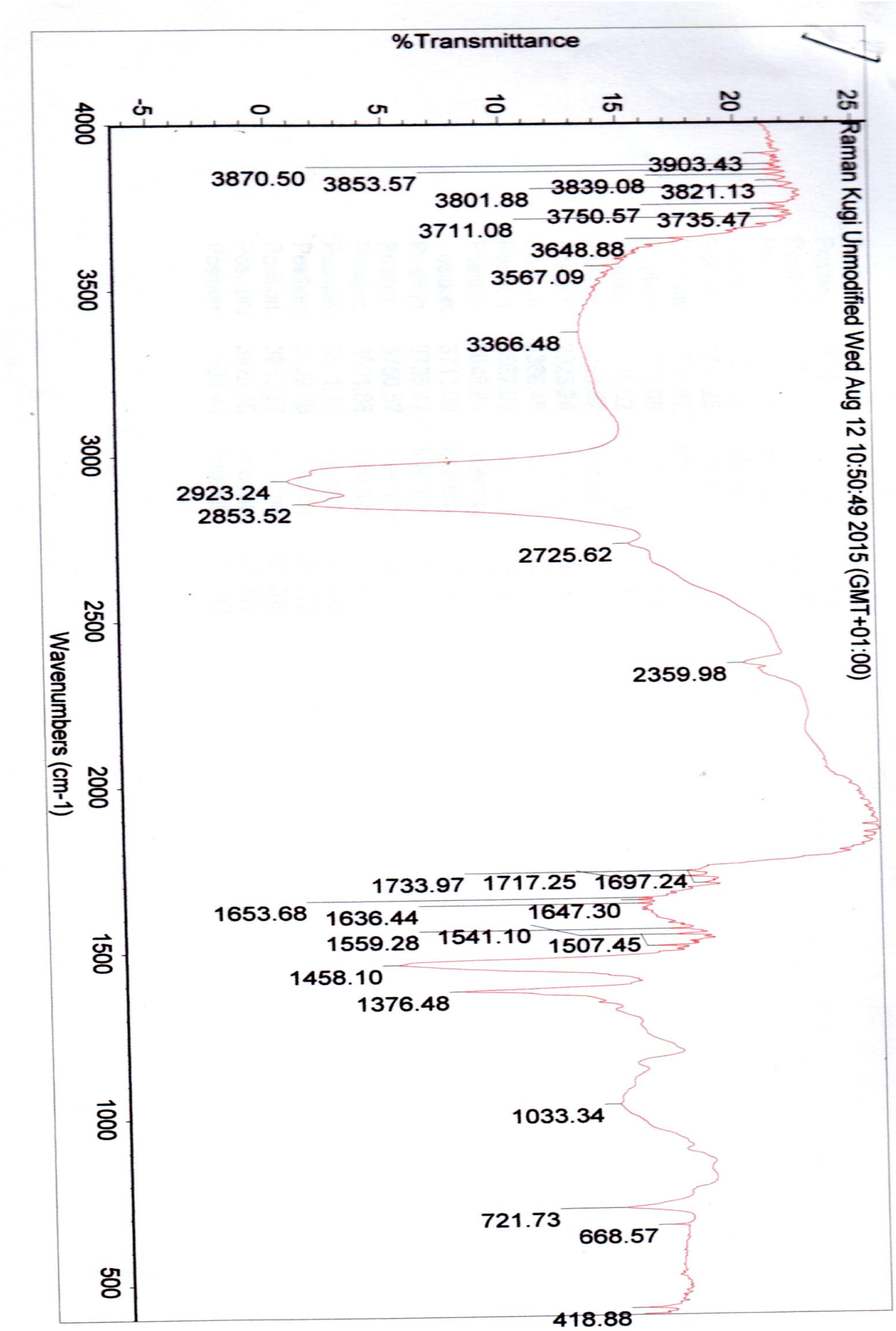

Figure 2. FT IR spectra of unmodified *Hibiscus asper*

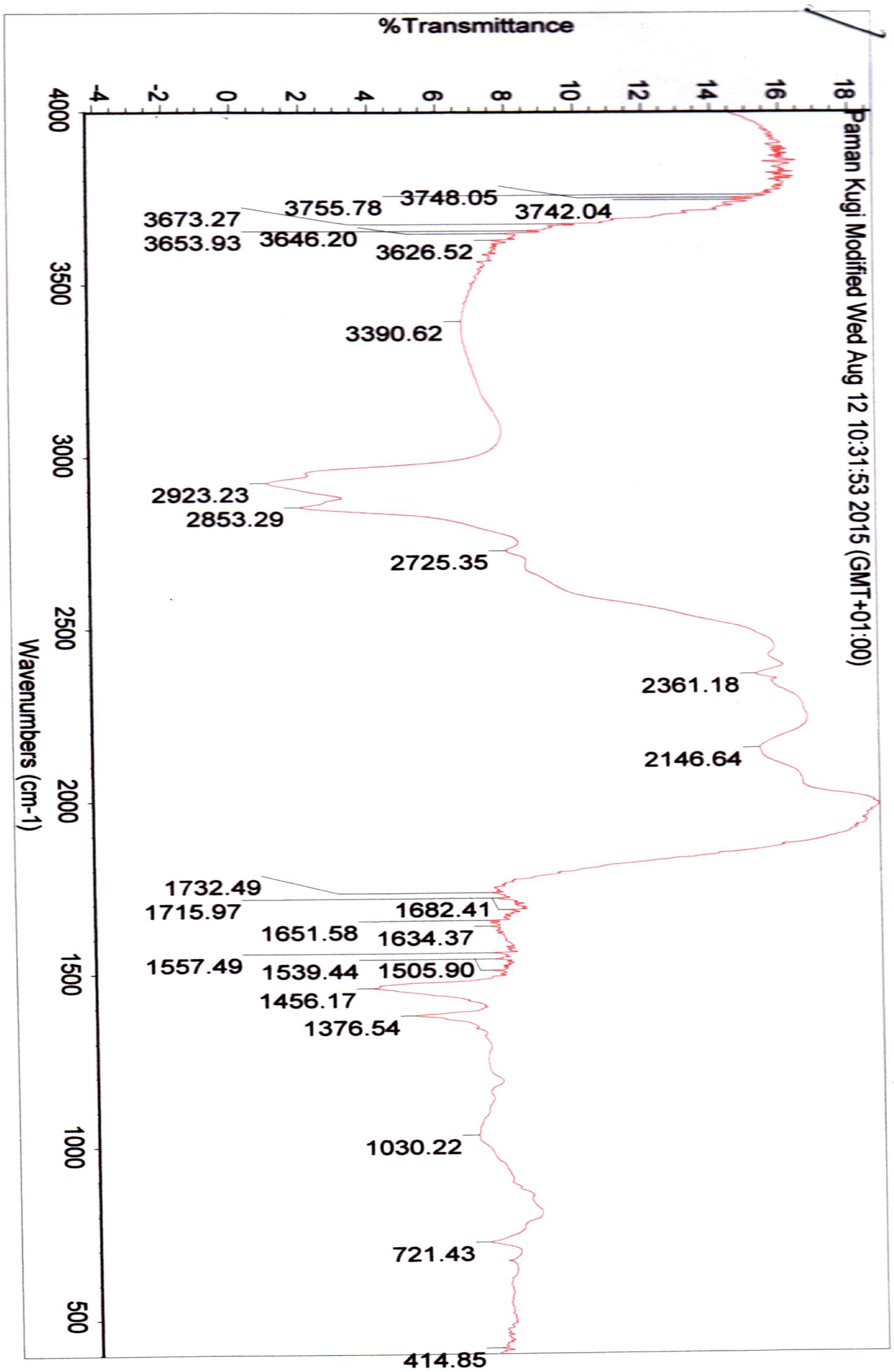

Figure 3. FT IR spectra of modified *Hibiscus asper*

CONCLUSION

In these research work the use of acetylated natural plant materials (*Hibiscus asper*), as sorbents for eliminating spilled oil from water bodies has been studied, the sorption behavior of the acetylated natural plant materials has indicated the hydrophobic status of the modified sample. Acetylation of the natural plant materials in the presence acetic anhydride using calcium chloride as catalyst in a solvent free system has proven to be successful.

The sorbents fitted the Langmuir model best the isotherms produced the highest correlation coefficient (R^2). That means the model assumed monolayer coverage of the oil over the acetylated plant materials. The quick uptake and high absorption capacity makes the acetylated natural plant materials a good alternative sorbent for crude oil spill clean-up.

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