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Modification, Characterization and Use of *Imperata cylindrical* (Toofa) Fibre as Oil Sorbent

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

The effect of Acetylation on *Imperata cylindrical* fibre using acetic anhydride was 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°C for 3 hour. The crude oil and the *Imperata cylindrical* 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 *Imperata cylindrical* sorbent to further examine the success of acetylation. In the spectra of FT-IR of the acetylated *Imperata cylindrical* 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 *Imperata cylindrical* 1.00) better than the Freundlich isotherm, indicating that the adsorption process was monolayer. The higher oil sorption capacity shown by the modified *Imperata cylindrical*

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sorbent compared to the lower oil sorption capacity of unmodified, indicated that the modified *Imperata cylindrical* sorbent can substitute for synthetic fibres and recommended for oils spill clean-up in contaminated environments.

Keywords: Adsorption; oil spill; sorbents; Imperata cylindrical; fibre; langmuir isotherm.

1. 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 [1]. Oil spills commonly occurs today was 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 [2] 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%) [1].

Sorbents are insoluble materials or mixtures of materials used to recover liquids through the mechanism of absorption or adsorption or both. Materials must be both hydrophobic (repel water) and oleophilic (attract oil) [3].

However, as long as the oil continues to floats over the surface of the water it harms aquatic life, pollute the water and damage the land and as such cleaning the oil spill is very important. Various commercial systems were developed to control these spills which include the use of brooms, dispersants, skimmers, oil water separator or different kinds of sorbent materials [4].

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 [5,6,7,8,9,10]. 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. Toofa consist of cellulose 95%, hemicellulose 2%, peptins 2% and extractives 1% while the characteristics functional group is –OH [11]. 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 [11] 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 researches have 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 such as Rice Husks [8,12].

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.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

Toofa fibre was obtained from toofa plant (*Imperata cyclindrical*) Fig. 1. The plant part 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 plant part 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°C in the oven then later stored in a labeled polyethene bags. The crude oil sample was collected in a sample bottle from Port-Harcourt Refinery in River State, Nigeria.

2.2 Extraction Procedure

5 g of Toofa bark was extracted with the mixture of ethanol-toulene (2:1 v/v) for 3 hours. After

Fig. 1. Picture of *Imperata cyclindrical* (Toofa) plant

extraction the samples was rinsed with ethanol followed by hot water and oven dried at 105°C for 24 hours to reach a constant weight. The extractible content was calculated as a percentage of oven dried test samples.

2.3 Chemical Modification

The acetylation was carried out in mild conditions in the presence of calcium chloride using acetic anhydride by [11] in a free solvent system. 5 g of sample was placed in a 500 ml flat bottom flask containing 300 cm^3 of the acetic anhydride and 30 g of calcium chloride. The flask was placed into a thermostatic water bath set at 100°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°C for 8 hours. The dried modified toofa fibre was re-weighed to determine the weight gain on the basis of initial oven dry measurement, weight percent gain % (WPG) of the toofa fibre due to acetylation was calculated from the formula below:

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

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

2.4 Characterization of the Sorbents

Moisture content

The moisture content was determined according to the method of [13].

Ash content

Ash content was determined using the methods employed by [14,15].

Volatile content

The Volatile content was determined according to the method of [16].

Fixed carbon

The fixed carbon was determined as adopted by [16].

Bulk density

The method described by [17] was adopted.

Porosity

This was determined by the method adopted by [17].

Specific gravity

The method of Bureau of Indian Standards [17] was adopted.

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

The swellabilty and anti-swelling activities were determined as adopted by [17].

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 [12].

Viscosity

The viscosity of the crude oil was obtained using a viscometer at 25°C.

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 0.998 g/dm3.

The American Petroleum Institute (API)

This was obtained using the method describe by [12].

2.5 Crude Oil Sample Weathering

The crude oil contains low boiling fractions that evaporate after a spill and this often occur before significant cleanup operations can take place. In the early stages of an oil spill, lighter hydrocarbons evaporate and consequently the viscosity of the oil increases before any possible cleanup operations 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.

2.6 Oil Sorption Studies

20 ml of oil sample was transferred in 150 ml of water in a 250 ml beaker, different weights of the plant material were spread on the surface of the mixture, the procedure was repeated at room temperature, after 20 minutes, the plant materials were 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

2.7 Determination of the Amount of Water Sorption

The water content of the sorbent was determined in the laboratory using the method of centrifuge technique described by [8]. The plant material was subjected to pressing to desorb the crude oil. During the pressing stage petroleum ether (10-20 ml) 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.

2.8 Fourier Transform Infrared Spectroscopy Analysis (FT-IR)

The modified and unmodified properties of toofa 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.

2.9 Statistical Data Analysis

The data obtained was analyzed using the method for calculating mean and standard deviation by Gary (2004) expressed as estimate standard deviation S of a finite set of experimental data (N< 30) at 95% confidence level and two degrees of freedom.

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

3. RESULTS AND DISCUSSION

The results of the physico-chemical properties of the unmodified and modified plant materials are shown in Table 1. The results shown that during

Table 1. Physico-chemical properties of unmodified and modified Toofa samples

Characterizing properties	Unmodified	Modified
Ash Content (%)	6±0.01	7±0.01
Moisture content (%)	8±0.01	50±0.01
Volatile content (%)	86±0.01	3±0.01
Bulk Density (g/cm^3)	1.21±0.01	1.19±0.01
Fixed Carbon (%)	8±0.01	60±0.01
Specific Gravity (g/cm^3)	0.020±0.01	0.019±0.01
Sweallability (Absorption)	631±0.02	740±0.01
Oil Sorption Capacity (%)	500±0.02	509±0.02

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 Toofa has the ash content of 7%, moisture content of 50%,. The swellability was 631%. The result is in tanden with results obtained by [12] on other fiber materials. The oil sorption capacity was 509%, this shows that the acetylation of the plant materials makes it a possible sorbent for oil spill application [12]. The improvement and changes in the properties of the plant materials after acetylation is an indication of a successful acetylation, the WPG was 35%.

The physico-chemical 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 shows its lightness in the recorded density of less than 1 and specific gravity which makes a promising sorbent, the viscosity at 30°C is 3.06 mpa.s, these properties tend to affect the way oil samples are being absorbed by the sorbents.

The reaction temperature plays a vital role on the effect of Acetylation (Sun, et al. 2004). 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 toofa and the weight per gain is illustrated in Table 3. The WPG at 60°C increases up to 4.6 at 60 Mins then decline at 80 mins. This result agreed with the work done by [12], where acetylated rice husk showed increased in weight per gain with increased temperature during modification.

Table 2. Physico-chemical properties 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°C)	35.07±0.01
Viscosity (30°C, mpa.s)	3.06±0.01
Ash content (%) @ 700°C	11.80±0.01

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

The oil/water sorption ability of the natural plant materials was examined in order to understand the sorption capacity of the sorbents. 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 result

Table 3. The effect of temperature and time of Acetylation of Toofa

Time (min)	Temperature (OC)				
	10°C	20°C	30°C	40°C	60°C
	WPG%				
10	1.7	2.0	2.3	2.5	2.7
20	2.1	2.3	2.6	2.8	3.0
30	2.4	2.6	2.9	3.1	3.5
40	2.8	3.2	3.4	3.6	3.8
50	3.2	3.4	3.6	3.8	4.1
60	3.0	3.6	3.8	4.0	4.6
80	2.4	2.7	2.9	3.7	4.0
100	1.8	2.0	2.5	3.0	3.5
120	1.6	1.8	2.0	2.8	3.0

of the oil and water sorbed by unmodified and modified toofa is shown in Table 4. The higher sorbed oil/water by modified plant materials is a proof of hydrophobic nature with low water uptake, reduction in water sorbed along with oil due to hydrophilic tendency of the unmodified sorbent; this also showed similar result by [8] with barley straw which reported low water sorption ability.

The oil sorption capacity recorded by the natural plant materials is shown in Table 5. The unmodified oil sorption of toofa 11.55 g/g to 21.93 g/g compared to modified 18.30 g/g to 37.59 g/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.

Water sorption capacity was examined to understand the water sorption ability of the sorbent and the results are shown in Table 6. The unmodified plant materials showed higher water uptake at 60 minutes compared to water uptake by the modified.

Water uptake by unmodified toofa 0.75 g/g to 3.42 g/g, While water uptake for modified increased from toofa 0.33 g/g to 1.89 g/g. Modification was achieved by acetylation which resulted in less water uptake by the modified plant materials.

Table 4. Oil and water sorbed by unmodified and modified Toofa samles

Weight of sorbent (g)	Sorption time (Mins)	Oil and water sorbed sorbed (Unmodified g/g)	Oil and water (Modified g/g)
0.5	60	8.73	9.51
1.0	60	10.68	12.15
1.5	60	14.52	17.61
2.0	60	17.91	20.91
2.5	60	18.99	22.83

Table 5. Oil sorbed by unmodified and modified Toofa samples

Weight of sorbent (g)	Sorption time (Mins)	Oil sorbed (Unmodlfied g/g)	Oil sorbed (Modified g/g)
0.5	60	11.55	18.30
1.0	60	12.66	24.99
1.5	60	16.05	32.82
2.0	60	20.13	34.29
2.5	60	21.93	37.59

Table 6. Water uptake capacity by unmodified and modified Toofa sample

Weight of sorbent (g)	Sorption time (Mins)	Water uptake (Unmodified g/g)	water uptake (Modified g/g)
0.5	60	0.75	0.33
1.0	60	1.44	0.72
1.5	60	1.83	1.02
2.0	60	2.43	1.23
2.5	60	3.42	1.89

Table 7. Effect of 1 g acetylated reusability of Toofa sample

Weight of sorbent (g)	No. of cycles	Sorption time(Min)	Oil sorbed (g/g) TF
1	1	60	7.05
1	2	60	11.13
1	3	60	12.42
1	4	60	12.03
1	5	60	11.82

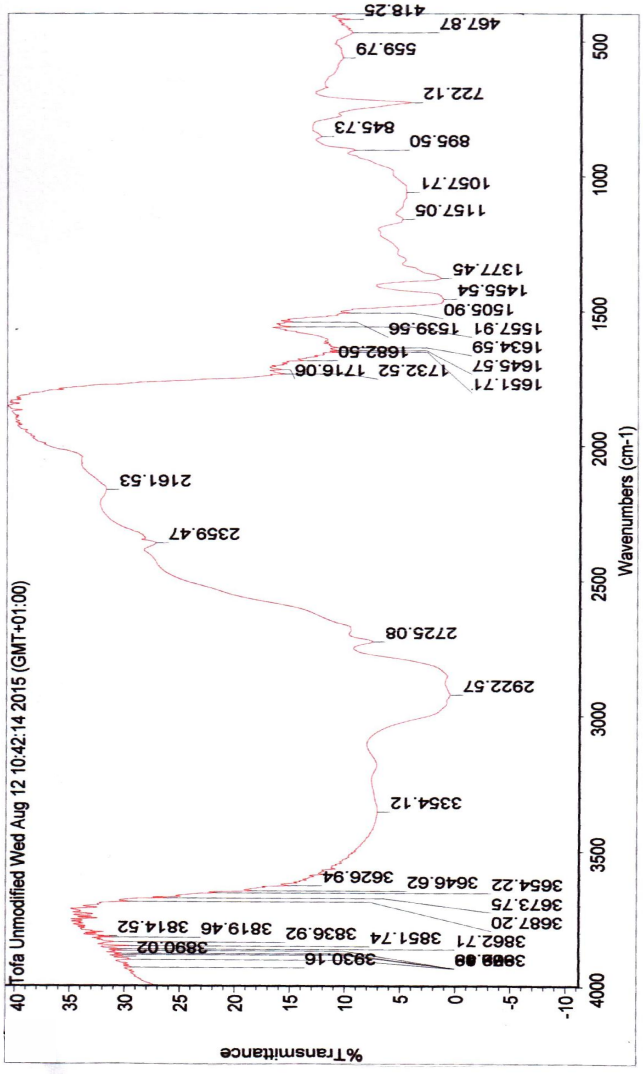

Fig. 2. FTIR spectra of unmodified Toofa

The effect of reusability was carried on crude oil as shown in Table 7. The result showed that the acetylated toofa, 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.

The effect of time on the modified toofa (Table 8) showed that sorption capacity increased with increased sorption time, this result agreed with related work by [8]. Sorption qualities of barley strands, both revealed increased time with increased sorption time. The result showed that the oil sorbed by toofa to increase from 2.55 g/g to 3.91 g/g.

Table 8. Effect of sorption time on 1 g of Toofa sample

Weight of sorbent (g)	Sorption time (Min)	Oil sorbed (g/g)
1	20	2.55
1	30	3.12
1	40	3.56
1	50	3.75
1	60	3.91

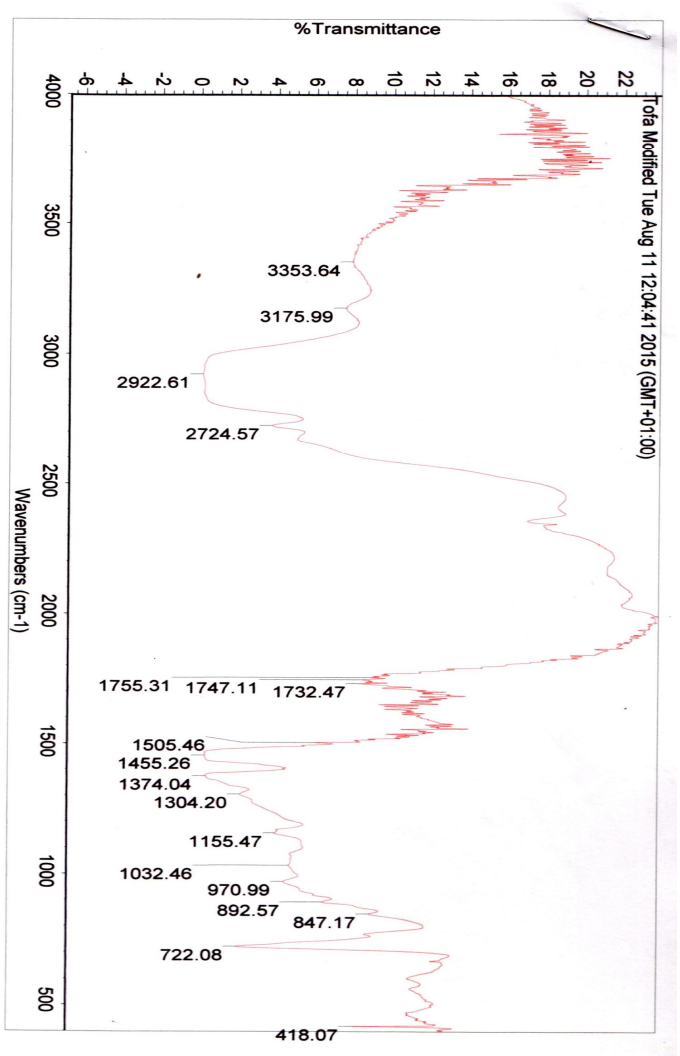

Fig. 3. FTIR spectra of modified Toofa

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 Table 9, k = 0.10, n = 0.42 and R^2=0.14. For Langmuir value Table 10, a = 0.2, b = 0.02 and R^2 = 1.00. These results showed that acetylated plant materials fitted Langmuir model isotherm for it has the highest R^2 value Table 11, 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, this makes it more suitable as oil sorbent compare to other agro-bases materials.

In the spectra of FT-IR of the acetylated plant materials 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 FT-IR spectra also proven the occurrence of successful acetylation of toofa in the presence of calcium chloride as a catalyst. The enhanced carbonyl peaks at C=0 ester (1755.31-1715.97), C-H absorption (2923.23-2146.60), C-O (1494.97-1403.35) stretching confirmed the formation of ester bonds. These peaks were observed to be absent in the spectra of unmodified natured plant materials. The FT-IR also proved sufficient for detecting the extent of acetylation and the performance of acetylated products.

Table 9. Freundlich isotherm of Toofa

Log Ce	log Qe
- 0.03	1.26
1.00	1.40
0.18	1.52
0.30	1.54
0.40	1.60

Table 10. Langmuir isotherm of Toofa

Ce/Qe	Ce
0.03	0.5
0.04	1.0
0.05	1.5
0.06	2.0
0.07	2.5

Table 11. Tables of the Langmuir and Freundlich isotherms model constant

	Langmuir model			Freundlich model		
	a	b	R2	k	n	R2
Toofa	0.20	.02	1.00	0.10	0.42	0.14

4. CONCLUSION

In this research work, acetylation of toofa fibre using calcium chloride was successful. The oil sorbed can be easily removed from natural plant materials sorbents by mechanical squeezing operation. The desorption studies for the recovery of the crude oil from the acetylated natural plant materials sorbents using petroleum ether as solvent demonstrated the recycling of these sorbents and reused in another round of crude oil clean-up operations. They can be reused up to 4 times while the acetylated sorbents can be reused about 3 times. When the oil is removed the acetylated material can be disposed of without any environmental hazard Results obtained in the sorption studies indicated that the modified toofa fibre had lower water sorption than the unmodified, this implied that the modified toofa fibre had lower hydroscopicity with high hydrophobicity and the R^2 value of 1.00 model assumed monolayer coverage of oil over the acetylated toofa fibre, this makes the toofa fibre a good alternative sorbent for oil spill clean-up, in addition to its availability and cheap

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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