SORPTION, REMEDIATION AND KINETIC MODELING (LIQUID FILM DIFFUSION) OF CRUDE OIL SPILLS ON SURFACE WATER WITH A MODIFIED (ACETYLATION) AND NATURAL FIBERS OF SANSEVIERA LIBERICA (AFRICAN BOWSTRING HEMP).

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Abstract

Application of acetylated and natural Sansiviera liberica (SL) fibers has been investigated for their sorption capacities in the remediation of oil spills on water bodies. Extracted SL fibers were selectively characterized by moisture content (39.32%), crude fiber (73.03g), ash content (8.73g), dry matter (37.32g) and crude lipid (0.16g). The crude oil sample was of the characterizations by dark brownish appearance, specific gravity (0.84g/cm3), sulphur content (0.79%),Viscosity (12.73 MPa at 25oC) and American petroleum institute gravity (API) of 26.50.FTIR characterizations of the acetylated and natural SL fibers were analyzed with the confirmation of hydroxyl groups(-OH) of the cellulose in the natural SL fiber matrices to have been successfully substituted with acetyl (-CH3O) group after acetylating at 85oC and 90 minutes. The oil sorption capacities of both acetylated and natural SL fibers were observed to maintain direct proportionality with the time factor (kinetics). The liquid film diffusion (LFD) as the kinetic model with the sorption mechanisms between the acetylated and natural SL fibers was expressed as (R2=0.922; intercept=0.918) and (R2=0.881; intercept=0.716) respectively.

The two independent sample T-test with the two categories were concluded to be significantly different with the test under equal variances (One tail) to have Tstatistic (4.37726506) > Tcritical (1.73406); (Two tail) having T statistic (4.37726506) > Critical (2.10092) and with unequal variance (One tail) with Tstastistic (4.37726506) > Tcritical (1.77093); (Two tail) having Tstatistic (4.37726506) > Tcritical (2.16037)..

Keyword: Sansiviera liberica, plant fiber, crude oil, acetylation, liquid film diffusion.

1.INTRODUCTION

Oil is one of the most fundamental energy resource and crude material for the manufacture of polymers and synthetic compounds [1]. For whatever length of time that oil is investigated, shipped and utilized, there will be the danger of spillage. Oil contamination, especially

of ocean and traversable waters, has a more open threat than other nature of wastes.

Oil contamination of the ocean has dynamically expanded with the expanded oil utilization. The all-out yearly inundation of oil from hydrocarbons is around million metric tons in the US [2]. The main part of this spill is due to transportation-related exercises from tanker stacking and transferring activities, pipeline leakages and spillage from automobiles. Oil contamination of the shore, notwithstanding the decline of some important resources, influences marine, shore life and vegetation adversely. [3]. Crude oil comprises of various hydrocarbons that range from a light gas to substantial solids. At the point when oil is spilled on water, the physical and synthetic properties of oil change dynamically, for example, these physicochemical changes accelerate oil disintegration in seawater [4]. Concerning this challenge, different procedures have been designed to expel oil from tainted territories by the use of blasts, dispersants, and skimmers, oil-water separators or by utilization of various types of sorbent material [5]. Oil sorbents material can be sorted into three significant classes: natural vegetable items, inorganic mineral operators and natural manufactured items [6]. Among manufactured sorbents which can be used, polypropylene nonwoven sorbents have high oil sorption limit and low water take-up and subsequently, polypropylene nonwoven sorbents are perfect materials for oil recuperation from the water surface. Past investigations show that mechanical recuperation is the exchange of oil from the spilled territory to some transportable type of transitory stockpiling by the backing of oil sorbents or skimmers [7]. It is as of late assessed that the permeable materials utilized for oil slick cleanup and a few investigations of various characteristic, engineered and mineral sorbents have additionally been led [8],[9] delivering a free stringy material which is oleophilic, hydrophobic and floatable on water for specific ingestion of hydrocarbons[10]. Most generally commercial sorbents are manufactured sorbents made of polypropylene or polyurethane [11]. They have great hydrophobic and oleophilic properties, however, they are not biodegradable [12]. A biodegradable material with fantastic assimilation properties would be profitable in this regard. Various normal sorbents have been applied in oil slick cleanup, for example, cotton and bark which can be great oil sorbent given its hydrophobic and oleophilic character [13]. Cellulosic sorbent has been artificially treated. Sugarcane bagasse was esterified with acidic anhydride with N-bromosuccinimide as a force under gentle conditions [14]. The acetylation technically expanded hydrophobic properties of the bagasse and the oil sorption limit of the acetylated bagasse acquired at 80ºC for 6 h. Adebajo and Frost, (2004) examined the acetylation of cotton to create hydrophobic, biodegradable cellulosic materials for resulting application in oil slick cleanup [15]. At last, Edyta et al. (2003)[16] reasoned that the contact edge of oil on wet new straw for the outer surface of the stalk and leaf is over 150°C which demonstrates that these surfaces are oleophilic in a fluid situation. In a bid to engineer an agro-based, oleophilic, hydrophobic and biodegradable sorbent material, fibrous plant biomass; Sanseviera liberica was adopted.

Sansevieria liberica has been developed in Nigeria for its leaf strands (fibers) that were utilized for making ropes, bowstrings and angling lines [17].Strands (fibers) are as well utilized for stringing, decorations and to make wipes. The fiber needs unique treatment which has limited its business use. However, there is a gap to objectively evaluate the possibility of applying an enhanced fibrous, oleophilic and hydrophobic plant biomass in the removal or remediating oil spilled contaminated water body (ies).

2.MATERIALS AND METHODS

2.1. Sorbent material collection, fibers extraction and characterization

The plant sample was harvested within the Institute (NARICT, Zaria Kaduna State, Nigeria) and was confirmed by plant physiologist from Ahmadu Bello University Zaria Kaduna State, Nigeria.

The stem was detached and striped to expose the fibrous portion. It was thoroughly washed with water to remove dust and other foreign materials. It was then dried in an oven at 80°C for 2 h for complete removal of water, ground and selectively blended into 250um mesh size. Moisture content [18], ash content [18], crude fiber [19], dry matter [18] and crude lipid [20] were evaluated and stored in a zip lock polyethylene for subsequent use.

2.2. Crude oil sample characterization

The crude oil sample was gotten from NNPC Kaduna refinery. It was characterized for colour, specific gravity [21], API gravity [22], viscosity [23] and sulphur content [24].

2.3. Acetylation (Modification) of SL fibre

This process was conducted in the presence of N-bromosuccinamide (1.5%), 150ml of acetic acid with 5g of SL fibers in a 250ml conical flask. The reaction was refluxed at 120oC for 90minutes under atmospheric pressure. The reaction was filtered and thoroughly washed with ethanol/acetone mixture (60:40) to completely remove unreacted acetic acid. The acetylated SL fibers were oven-dried at 60oC for 8 hours [25].

2.4. Crude oil sorption capacity of an acetylated and natural SL

Simulating the nature of crude oil spill, crude oil sample was exposed for allowing the escape of volatile fraction. 500ml of artificial seawater (3.5 % NaCl) was placed in a 1 L beaker. 40 g of oil was added to the beaker container. 2.0g of sorbent was carefully wrapped with 0.8g of sieve clothes and dispersed over the surface of the crude oil solution. The beaker containing the oil sample and the artificial seawater was mounted in a shaker which was shaken for 10 min at 105 cycle /min. The bath temperature was kept constant at 25 ± 1°C using a thermostatic water bath. After 1 min, the fibers (sorbent) were moved vertically with net and the sorbent was left to drain by hanging the net on a retort stand. The method was repeated for 2, 3,4,5,6,7,8,9 and 10 minutes sorption periods [26]

2.5. Liquid film diffusion Model

The transportation of sorbate or the substrate molecules from the liquid phase through the surface of the biofilm (sorbent); the solid phase is enforced by laminar flow. It signifies the mass transfer between the flows from the liquid layer to the solid biofilm phase. According to Keith Kim Hung Choy ,2003, the liquid film diffusion model is presented as follows;

$$-\ln (1-F) = Kt$$

Where F is the ratio of the oil sorption capacity at a defined time (OSCt) to the capacity at equilibrium (OSCe) and K, the liquid film diffusion constant. A linear plot of –ln(1-F) against time(t) with zero intercept would suggest kinetics of the sorption process being controlled by diffusion through liquid film surrounding the solid sorbent while the intercept more than zero is an indication that the liquid film diffusion model is significantly controlled by the modification and kinetics of sorbent material.[27]

3.RESULTS AND DISCUSSION

Table I Characterization of SL fibers

Properties	Values
Moisture (%)	39.32
Crude fiber(g)	73.03
Ash content(g)	8.73
Dry matter(g)	37.32
Crude lipid(g)	0.16

Table II. Characterizations of crude oil sample.

Parameters	Values
Colour	Dark brown
Specific gravity (g/cm3)	0.84
API (25°C)	26.5
Sulphur content (%)	0.79
Viscosity (25°C,Mpa)	12.73

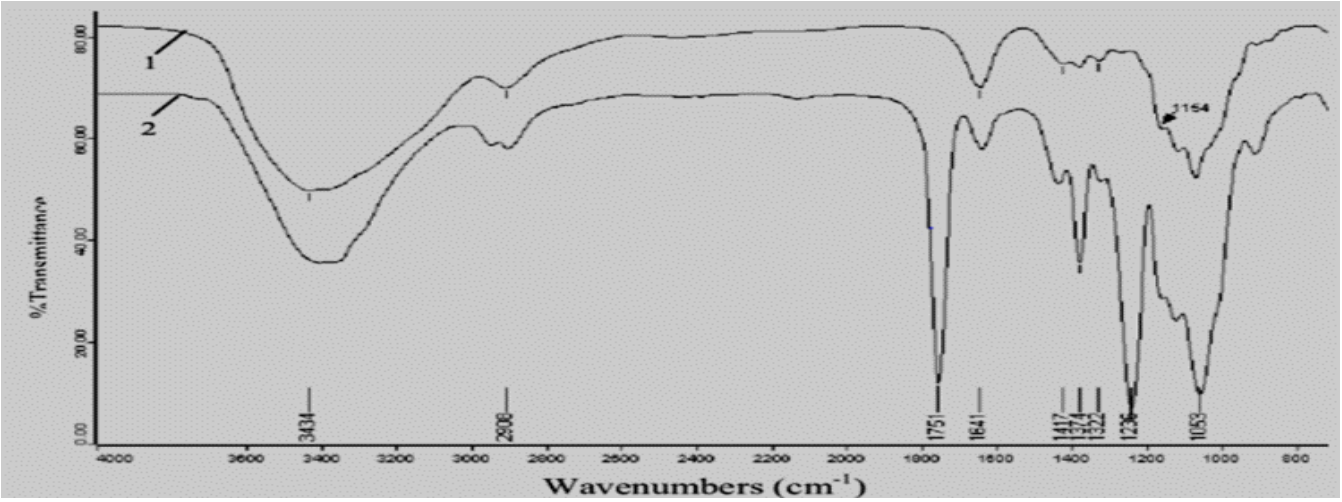

Figure l. FTIR spectrum of acetylated (2) and natural (1) SL fiber.

Table lll. Oil sorption capacities (OSC) with acetylated and natural SL fibers.

Acetylated				Natural		
Time(min.)	OSC/2.8g sorbent hybrid	Oil sorbed(g)	% OSC	OSC/2.8g sorbent hybrid	Oil sorbed(g)	% OSC
1	2.92	0.12	4.29	2.82	0.02	0.71
2	2.96	0.16	5.71	2.85	0.05	1.79
3	3.25	0.45	16.07	2.93	0.13	4.64
4	3.30	0.50	17.86	2.96	0.16	5.71
5	3.34	0.54	19.29	2.98	0.18	6.43
6	3.37	0.57	20.36	3.03	0.23	8.21
7	3.39	0.59	21.07	3.05	0.25	8.93
8	3.42	0.62	22.14	3.07	0.27	9.64
9	3.42	0.62	22.14	3.09	0.29	10.36
10	3.42	0.62	22.14	3.09	0.29	10.36

Table lV. Liquid film diffusion (LFD) model of acetylated and natural SL fibers.

Acetylated				Natural		
Time(min.)	F=OSCt/OSCe	1-F	-In (1-F)	F=OSCt/OSCe	1-F	-In (1-F)
1	0.85	0.15	1.92	0.91	0.09	1.92
2	0.87	0.13	2.00	0.92	0.08	2.01
3	0.95	0.05	3.00	0.95	0.05	3.00
4	0.97	0.04	3.35	0.96	0.04	3.35
5	0.98	0.02	3.76	0.96	0.04	3.76
6	0.99	0.02	4.22	0.98	0.02	4.23
7	0.99	0.01	4.74	0.99	0.01	4.74
8	1.00	0	0	0.99	0.01	0
9	1.00	0	0	1.00	0	0
10	1.00	0	0	1.00	0	0

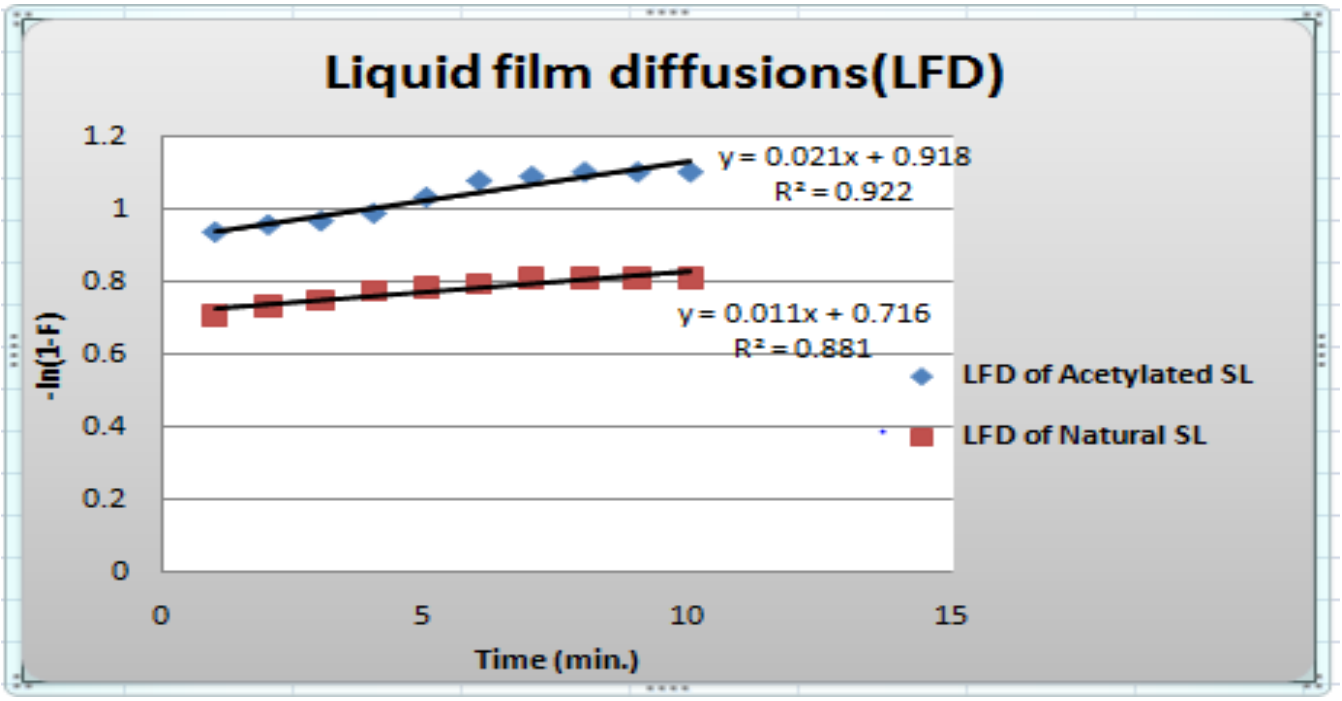

Figure ll. Liquid film diffusions (LFD) of modified (acetylated) and natural SL fibers

Table V. T-test two independent samples (acetylated and natural SL fibers).

Time(min.)	Acetylated SL fiber	Natural SL fiber
1	2.92	2.82
2	2.96	2.85
3	3.25	2.93
4	3.30	2.96
5	3.34	2.98
6	3.37	3.03
7	3.39	3.05
8	3.42	3.07
9	3.42	3.09
10	3.42	3.09

T Test: Two Independent Samples									
SUMMARY			Hyp Mean Di	0					
Groups	Count	Mean	Variance	Cohen d					
Acetylated SL	10	3.279	0.0351						
Natural SL	10	2.987	0.0094						
Pooled			0.02225	1.95757245					
T TEST: Equal Variances				Alpha	0.05				
	std err	t-stat	df	p-value	t-crit	lower	upper	sig	effect r
One Tail	0.066708	4.37726506	18	0.00018164	1.73406			yes	0.71806
Two Tail	0.0667083	4.37726506	18	0.00036328	2.10092	0.151851	0.43215	yes	0.71806
T TEST: Unequal Variances				Alpha	0.05				
	std err	t-stat	df	p-value	t-crit	lower	upper	sig	effect r
One Tail	0.066708	4.37726506	13.4985	0.00034328	1.77093			yes	0.76595
Two Tail	0.0667083	4.37726506	13.4985	0.00068656	2.16037	0.1478854	0.43611	yes	0.76595

Table I is the characterization of the extracted SL fiber. Moisture content was 39.32% after complete dehydration at 102oC. Crude fiber at the level of 73.03g justifies the basis of adopting SL.

Ash content, dry matter and crude lipid as 8.73g, 37.32g, and 0.16g respectively qualify the plant's fiber sorption application. Table II is the selected physic-chemical properties of the crude oil sample. Ordinarily, the American petroleum institute gravity at ambient temperature (API gravity) which by standard measures the heaviness (< 10) and lightness (> 10) of the oil sample at 26.5 to be lighter and able to float readily. The sulphur content of 0.79% and viscosity of 12.73MPa at 25oC were estimated.

Figure I is the FTIR spectrum of both the natural (1) and acetylated (2) SL fibers which at the absorption peaks of 3434cm-1, 2906cm-1 and 1374cm-1 are indications of OH stretch, CH stretch and CH2/CH3 groups with the natural and unmodified SL fibers. While absorptions at 1236cm-1 and 1053cm-1 indicate the presence of C=O stretch from the H3C=O group which is the acetyl group achieved from acetylating the SL fiber which technically eliminates the OH groups.Table III is the oil sorption capacities (OSC) of the acetylated and natural unacetylated SL fibers. The OSC with regards to the residence time of the wrapped sorbent in the water-oil system was enhanced with 2.0g of the SL fibers (acetylated and natural) and 0.8g of sieve clothe which serves as a binder to the fibers allowing a uniform dispersion with the water-oil mixture.

Liquid film diffusion (LFD) model of the acetylated and natural SL sorbent against crude oil as expressed in table IV is a kinetic model that expresses the mobility of the sorbate (crude oil) against the surface of the sorbents concerning time. Figure II further revealed the plot for this kinetic model with acetylated (R2=0.922; intercept=0.918) and natural (R2=0.881; intercept=0.716) SL fibers.

The regression coefficient (R2) and the intercept with acetylated SL fiber are higher than that of natural SL fiber as the regression reflects the relationship between the sorbate and the sorbent, while the intercept is the activity of the sorbent material involved in the sorption mechanism.

Table V is the two independent sample T-test between oil sorption capacities (OSC) of acetylated and natural SL fibers under the control of time (1, 2, 3,4,5,6,7,8,9 and 10min.).

The average mean of the OSC with the acetylated and natural SL fibers is 3.279 and 2.987 respectively. The Tcritical (1.73406) is less than the Tstatistic (4.37726) with one tail equal variance and with the two tail equal variance, Tcritical (2.10092) which is also less than the Tstatistic (4.37726). With unequal variances and one tail, Tstatistic (4.37726) is higher than the Tcritical (1.77093) while two-tail unequal variance; Tstatistic (4.37726) higher than the Tcritical (2.16037).

4.CONCLUSION

Natural plant fibers have been discovered with the potential of been employed as biosorbent material simply because of their level of fibers. Sansevieria liberica has not been an exception with the sorption of crude oil in an oil-water system. Meanwhile, the sorption capacities were enhanced and improved with the modified (acetylated) SL fibers than to the natural SL fibers.

As well, the kinetic modeling of oil sorption mechanism with acetylated and natural SL fibers in terms of liquid film diffusion revealed the relationship between the sorbate(crude oil) and the sorbent(SL fibers) to be much closer. The total sorption outcomes with SL fibers with crude oil implies the possibility and likelihood of adopting modified plant fibers in the remediation of oil spill on water bodies.

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