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# **Extension of Comparison of the Mopping Ability of Chemically Modified and Unmodified Biological Wastes on Crude Oil and Its Lower Fractions**

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*Authors' contributions*

*This work was carried out in collaboration between all authors. Author JKN designed and wrote the entire manuscript including corrections to the reviewers comment, author VIU sourced the whole materials while both carried out the entire laboratory work. All authors read and approved the final manuscript.*

*Research Article*

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# **ABSTRACT**

**Aim**: Is to extend our study on the number of locally available sorbents that can be used in oil/chemical spill clean-up.

**Study Design**: Carbonized and uncarbonized sorbents were separately encased in a sac like booms of 2cm x 2cm x 1cm dimension and used to mop up spills of different hydrocarbons.

**Place and Duration of Study**: Carbonization of sorbents was carried out at Federal Science Equipment Development Institute Enugu in Enugu State, Nigeria while the rest was done at Mechanical Engineering workshop, Nnamdi Azikiwe University Awka, Anambra State Nigeria between March –May 2011.

**Methodology**: Activated and unactivated powders of protein wastes (feather, goat hair) and cellulosic wastes (coco-nut husk, corn-cob), separated into two particles sizes of 325µm and 625µm were used to mop up spilt crude oil, diesel, kerosene and petrol and each were allowed a contact time of 30, 60, 90 and 120 mins contact time before they were hung in air to drain unabsorbed liquids. Recovery was carried by mere pressing, differences in weight were obtained and used for calculation of % absorption, recovery and

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retention.

**Results**: It was observed that all the sorbents mopped up appreciable quantities of all the sorbates within an average of 90mins contact time. Large volumes of the hydrocarbon liquids were recovered and retained, sorbates were mopped as- crude oil > diesel > kerosene > petrol, proteinous sorbents with oleophilic and aquaphobic properties absorbed more of all the hydrocarbon liquids than cellulosic sorbent at any particle size and contact time, although both showed high sorption capacity for the sorbates. Particle size of sorbents, activation, contact time, molecular chain length and viscosity of sorbates determined the amount of hydrocarbon absorbed/adsorbed, recovered or retained. The amount of residual leachable diesel in the sorbent was below 3%.

**Conclusion**: Sorbents studied showed high sorption capacity for the sorbates.

*Keywords: % absorption; % recovery; % retention; activation; particle size; oil/chemical spill.*

## **1. INTRODUCTION**

The Niger Delta region of Nigeria has had extensive environmental (air, soil and water) devastation due to several years of environmental degradation caused by crude oil related operations such as oil exploration (geographical investigation, drilling, platforms, tank farms and gas flaring), storage depots, transportation (pipelines networking and tanks) and oil processing (refining) [1]. All these release several million barrels of crude Oil and its fractional distillates into the ditches, streams, rivulets, ponds and rivers of the Niger Delta region of Nigeria. The U.S department of energy estimates that since 1960, there have been more than four thousand (>4000) oil spills in Nigeria's Niger delta region [2]. These has resulted in the destruction of interwoven freshwater aquifers, hampered the cultivation and bountiful harvest of rice, sugar cane, yams, plantains, cassavas, rubber and timber as well as fishing and hunting which are the natural occupation of the native people [3]. Planktons – the basis of marine food chain, including eggs and larvae of fish, aquaculture, fish and sea birds are also adversely affected [4]. Because of the fact that conventional clean up heavy equipment may not reach the creeks and river meanders of the Niger-delta because of its peculiar terrain, it becomes imperative to develop a cost effective means of containing (booming) and remediating (cleaning) oil spills that will not itself constitute environmental menace. Although several sorbents have shown promising results in oil/chemical spill control and containment in works such as experimental investigation of various vegetable fibers as sorbent materials for oil spills [5], oil adsorbent produced by carbonization of rice husks [6], efficiency of recycled wool-based nonwoven material for the removal of oils from water [7] and removal by sorption and in situ biodegradation of oil spills limits damage to marine biota, a laboratory simulation [8]. Also governing factors for motor oil removal from water with different sorption materials [9], evaluation of Kapok (*Ceiba pentandra* (L) Gaertn) as a natural hallow hydrophobic-oleophilic fibrous sorbent for oil spill cleanup [10] and use of biomass sorbents for oil removal from gas station run off [11] has all been investigated. A number of limitations (though not exhaustive) were inherent in them, most results and findings were for studies on a single sorbate [5,9], where several sorbents were used, they were used in their natural form (no activation) and for single sorbate [5], when carbonization was carried out, results were not compared with uncarbonized [6], effect of particle size (surface area) was not prominently discussed [11,12], also suitable environment for application was not reported [10,13,14]. It is an important fact that many biological materials (sorbents) which hitherto would have been waste is becoming economically useful, such as in fillers for polypropylene [15], in detoxification of  $pb^{2+}$  and  $cr^{3+}$  ions from solutions [16], in ensuring air quality [17] and in treatment of waste water [18].The sorbents of present study has shown more than 70% efficacy in purifying wastewater and the efficiency was greatly improved by activation [18]. In this work, our aim is to increase the number of such sorbents that can be used in oil/chemical spill clean-up and to minimize the limitations inherent in the previous studies.

### **2. MATERIALS AND METHODS**

#### **2.1 Materials**

#### **2.1.1 Collection of sorbents and preparation**

Cellulosic sorbents (corn cob and coconut-husk (coir) were procured from a local market around Awka in Anambra State, while protein sorbents (goat hair and chicken feather) were sourced from Awka main abattoir. They were thoroughly washed with soap solution, sun dried for two days before drying in an oven at 105ºC for 1hr and then ground, one half of each ground material was carbonized at a temperature of 300ºC for 30min, cooled and activated with  $1MH<sub>2</sub>SO<sub>4</sub>$  and further heated at a temperature of 500°C for complete carbonization. The carbonized materials were again pulverized. Both carbonized and uncarbonized materials were sieved into two particle sizes of 325µm and 625µm using mechanical sieve. Nylon 66 fabric whose adsorption profiles had been predetermined and found to be adequate was used for construction of pillow cases/bags (booms) of 2cm x 2cm x 1cm dimension for the sorbents [19].

#### **2.1.2 The sorbates**

Crude oil: [C (82%), H (15%), N (0.02%), O(0.5%)]: Diesel (C<sub>15</sub> – C<sub>20</sub>), Kerosene (C<sub>9</sub> – C<sub>15</sub>) and petrol  $(C_5 - C_9)$  were procured from Port Harcourt Refinery, Nigeria.

#### **2.2 Method**

Exactly 1.5g of the sorbents [(goat hair, chicken feather, corn-cob and coconut-husk (coir)] – both carbonized and uncarbonized and different particle size were separately encased in the pillow cases/bags, stitched and weight noted. Four (4) pillow cases/bags each for a given sorbent (coconut husk, corn cob, chicken feather, goat hair), both carbonized and uncarbonized for a particular particle size (325µm and 625µm) were introduced into the test liquid and completely immersed and withdrawn one after the other at 30, 60, 90 and 120mins intervals. Each pillow was hung in air for 5mins to drain off unabsorbed surface liquid. The quantity of liquid actually absorbed/adsorbed by the sorbents was determined by weighing. The amount of sorbate recovered was obtained by pressing the pillow at room temperature on a carver hydraulic press model M, Ser. No. 12000 – 137 at a pressure of 25 tonnes, for 3mins for sorbate – sorbent system. Average of three (3) operations was taken for adsorption and recovery for a particular test. From the results, the percentage absorption/adsorption, recovery and retention were calculated. The concentration of leachable oil was determined by soaking 3g of each sorbent with diesel(having previously determined that of crude oil) [19] for 1h, after which the oil was squeezed out, the squeezed sorbents was soaked in 10ml of warm xylene for 24hrs to extract the residual diesel from the sorbent. After filtration, the xylene layer was dried and the absorbance of the extract read on a UV-visible spectrophotometer at a wavelength of 420nm, the result compared well with a standard. This procedure was repeated at 48, 72 and 96hrs intervals [19].

### **2.3 Calculations**



% retention =  $%$  adsorption -  $%$  recovery

#### **2.3.1 Calculation for leachability test**

% leachability =  $100 - %$  retention % retention =  $A - B \times 100$ A

Where  $A =$  Initial concentration of leachable oil,  $B =$  Concentration of leachable oil after 24, 48, 72 and 96hrs.

 $A =$  Initial concentration of leachable oil = Weight after pressing  $-$  Weight before absorption/adsorption.

B = Concentration of leachable oil is the amount of oil still retained by the sorbents after initial 24, 48, etc extraction.

#### **3. RESULTS AND DISCUSSION**

#### **3.1 Results**

Table 1a: % absorption/recovery profiles by carbonized feather:

For carbonized at 325µm, highest absorption/recovery of crude oil is at 60/120mins, diesel at 120mins, highest absorption of kerosene is at 60mins while highest recovery is at 30mins contact time. Petrol was absorbed/recovered highest at 90mins.

Carbonized feather at 625µm, crude oil was sorbed/recovered more at 120mins, diesel was sorbed more at 30mins, 60 and 120mins (the same value for the three contact time) and recovered highest at 60mins. Kerosene was absorbed most at 120mins but recovered highest at 60 and 90mins respectively. Petrol was absorbed/recovered highest at 120mins.

Table 1b: % absorption/recovery profiles of sorbates by uncarbonized feather:

For 325µm, crude oil was absorbed/recovered highest at 120mins contact time; diesel, kerosene and petrol followed the same trend (highest absorption/recovery) at 120mins contact time.

For uncarbonized feather at 625µm, crude oil was sorbed/recovered highest at 120mins contact time, while that of diesel was at 90mins contact time, highest absorption/ recovery for kerosene and petrol occurred at 120mins contact time.

Table 2a: % absorption/recovery profile of goat hair:

For carbonized goat hair, at 325µm crude oil was absorbed/recovered highest at 120mins contact time; diesel was absorbed highest at 120mins time of contact but recovered most at 60mins. Kerosene was absorbed/recovered highest at 90mins; petrol was absorbed/recovered most at 120mins contact time.

Using particle size of 625µm, crude oil was absorbed highest at 120mins while highest recovery was at shortest contact time (30mins) diesel, kerosene and petrol were absorbed/recovered most at 120mins contact time.

Table 2b: % absorption/recovery profile of uncarbonized goat hair:

For uncarbonized goat hair, using 325µm, particle size, crude oil, diesel, kerosene and petrol were all absorbed/recovered highest at 120mins contact time.

Using 625µm goat hair (sorbent), crude oil, diesel and kerosene were absorbed/recovered highest at 120mins contact time while petrol was absorbed highest at 30mins but recovered most at 30mins and 90mins contact time respectively.

Table 3a: % absorption/recovery profile of sorbates by coconut husk:

For carbonized at 325µm, highest absorption/recovery of crude occurred at 120mins contact time, for diesel was 120mins and 30mins, kerosene the same 120mins and petrol at 90mins and 120mins.

For carbonized at 625µm, crude oil was sorbed and recovered highest at 120mins, that of diesel was at 120mins and recovery was at 60 and 120mins while kerosene and petrol were both absorbed and recovered highest at 120mins.

Table 3b: % absorption/recovery profile of uncarbonized coco-nut husk,

At 325µm highest absorption/recovery occurred at 90mins and 120mins for crude, diesel at 120mins and 90 and 120mins, kerosene at 30 and 120mins and petrol was absorbed and recovered highest at 120mins.

At 625µm particle size, highest absorption/recovery for crude occurred at 120mins, diesel at 120mins while that of kerosene and petrol occurred at 120mins respectively.

Table 4a:% absorption/recovery of sorbates by corn cob

Carbonized:

For 325µm particle size, highest % absorption at 120mins contact time while highest recovery was at 60mins contact time for crude oil, highest absorption at 60mins but highest recovery at 30mins for diesel. Kerosene's highest absorption was at 120mins while highest recovery was at 60mins. Highest % absorption/recovery for petrol was at 120mins. Averagely highest absorption/recovery occurred at 120min with a gradual decrease in absorption/recovery across the table (horizontal). For 625µm particle size, the same trend was observed though intermittent variation occurs due to forces of absorption and desorption.

Table 4b: 325µm uncarbonized, slightly lower percentage absorption and recovery were recorded for uncarbonized corn-cob at a given particle size and contact time for each sorbent-sorbate system. Highest absorption of crude oil was at 90mins contact time, while highest recovery was at 30mins contact time, for absorption/recovery, that of diesel was at 120mins time while recovery was at 90 and 120mins respectively. That of kerosene was at 60mins and 90mins, petrol was at 90mins.

For 625µm particle size highest absorption/recovery for crude oil was at 30mins contact time, diesel was at 120mins, kerosene was sorbed/recovered more at 60mins while petrol was sorbed more at 60mins and recovered more at 30mins.

All the above considerations were based on the initial oil mop  $(1<sup>st</sup>$  use), the same trend was observed at 2nd, 3rd and 4th use with minor variation.

Table 5: % retention profiles of sorbates by carbonized and uncarbonized feather at different particle size and contact time. When using 325µm particle size, averagely uncarbonized particle size and contact three. When doing croppin particle critically accepted from the retained crude oil highest than carbonized from 1<sup>st</sup> to 4<sup>th</sup> use with minor discrepancies. There was outright highest retention of diesel, by uncarbonized feather at all applications; the same scenario was observed in kerosene. Petrol was retained highest by uncarbonized feather at  $1<sup>st</sup>$  and  $2<sup>nd</sup>$  use while carbonized retained highest at  $3<sup>rd</sup>$  use and there was a near equal retention by both carbonized/uncarbonized at  $4<sup>th</sup>$  use.

Using 625µm particle size of feather, there exists variation in retention of crude oil by carbonized/uncarbonized feather at 1<sup>st</sup> and 2<sup>nd</sup> use while uncarbonized had highest retention at  $3^{rd}$  and  $4^{th}$  use. Uncarbonized retained diesel more at  $1^{st}$  and  $3^{rd}$  use while carbonized retained highest at  $2^{nd}$  and  $4^{th}$  use. Kerosene was averagely retained highest by uncarbonized feather from 1<sup>st</sup> to 4<sup>th</sup> use for all contact time. Reasonable percentages of fuel were retained by both carbonized/uncarbonized feathers at all applications with no definite direction.

Table 6: % retention profiles of carbonized and uncarbonized goat hair using 325µm, highest retention for both sorbents for crude oil occurred at 120mins, but at  $4<sup>th</sup>$  use, uncarbonized goat hair has highest % retention. For diesel, carbonized goat hair has highest retention at  $\tilde{1}^{\text{st}}$  use while uncarbonized goat hair had the highest retention from 2<sup>nd</sup> to  $\tilde{4}^{\text{th}}$  use. Kerosene was retained most by uncarbonized at 4<sup>th</sup> use. Petrol was retained highest by carbonized goat hair from  $1<sup>st</sup>$  to  $4<sup>th</sup>$  use.

Using 625 $\mu$ m, crude oil was retained highest by uncarbonized goat hair at 1<sup>st</sup>, 3<sup>rd</sup> and 4<sup>th</sup> use while carbonized retained more at 2<sup>nd</sup> use. Diesel was retained most by uncarbonized goat hair at 1<sup>st</sup> and 3<sup>rd</sup> use while carbonized retained highest diesel at 2<sup>nd</sup> and 4<sup>th</sup> application. Kerosene was retained highest by uncarbonized goat hair from  $1<sup>st</sup>$  to  $4<sup>th</sup>$  application while carbonized goat hair retained fuel most from  $1<sup>st</sup>$  to  $4<sup>th</sup>$  application.

Table 7: % retention of sorbates by carbonized/uncarbonized coco-nut husk at different particle size and contact time. Using coconut husk of 325µm, carbonized coco-nut husk retained highest crude oil at 1<sup>st</sup>, 3<sup>rd</sup> and 4<sup>th</sup> use while uncarbonized coco-nut husk retained highest at  $2^{nd}$  use. Diesel was retained highest by uncarbonized coco-nut husk in 1<sup>st</sup> 30 – 60 $m$ ins while carbonized retained it highest within 90 – 120 $m$ ins of 1<sup>st</sup> use. Uncarbonized retained it most in the 2<sup>nd</sup> use while carbonized retained most in 3<sup>rd</sup> and 4<sup>th</sup> use. Diesel was retained highest by uncarbonized coco-nut husk at 1<sup>st</sup> use at 30 and 60mins while carbonized retained it highest within 90 and 120mins of  $1<sup>st</sup>$  use. Uncarbonized retained it

most in the  $2^{nd}$  use while carbonized retained most in  $3^{rd}$  and  $4^{th}$  use. Kerosene was retained highest by uncarbonized coco-nut husk at first use while carbonized coconut husk retained highest at  $2^{nd}$ ,  $3^{rd}$  and  $4^{th}$  use. Petrol was retained highest by carbonized coconut husk at 1<sup>st</sup> and  $3^{rd}$  use while uncarbonized coconut husk retained it highest at  $2^{nd}$  and  $4^{th}$  use.

Using 625 $\mu$ m particle size, carbonized coco-nut husk retained crude oil highest at 1<sup>st</sup> use, uncarbonized retained highest at 2<sup>nd</sup> and 3<sup>rd</sup> use while there was near equal retention by both carbonized/uncarbonized at 4<sup>th</sup> use. Diesel was retained highest by carbonized coconut husk at  $1<sup>st</sup>$  use, uncarbonized retained highest at  $4<sup>th</sup>$  use while equal retention by carbonized/uncarbonized occurred at 2nd and 3rd use. No significant variation exists in the retention capacities of both carbonized/uncarbonized coco-nut husks for kerosene. For the petrol, uncarbonized coco-nut husk retained highest than carbonized for all the applications.

Table 8: % retention profile of sorbates by carbonized and uncarbonized corn-cob at different particle sizes and contact time.

Using 325µm, highest retention of crude oil by carbonized occurred at 90mins contact time while the uncarbonized retained highest at 120mins contact time, carbonized retained most at all application. Diesel was retained most by carbonized at 60mins while uncarbonized retained most at 90mins. Carbonized retained most at  $1<sup>st</sup>$  and  $2<sup>nd</sup>$  use while uncarbonized retained most at  $3^{rd}$  and  $4^{th}$  use. Highest retention of kerosene by both carbonized and uncarbonized occurred at 120mins contact time, but the uncarbonized retained more kerosene at 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> use. Petrol was retained most by carbonized at 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> use while uncarbonized retained most at first use.

Using corn-cob of 625µm, crude oil was retained most by carbonized at first use while uncarbonized retained it most at  $2^{nd}$ ,  $3^{rd}$  and  $4^{th}$  use. Uncarbonized corn-cob retained diesel most at first use while most was retained by the carbonized at  $2^{\text{nd}}$ ,  $3^{\text{rd}}$  and  $4^{\text{th}}$  use. Kerosene was retained most by uncarbonized corn-cob at 1<sup>st</sup>, 2<sup>nd</sup> and 4<sup>th</sup> use, carbonized retained highest at  $3^{rd}$  use. Fuel was retained highest by carbonized corn-cob at  $1^{st}$  and  $3^{rd}$  use. Uncarbonized retained most at 2nd use, equal retention of petrol by both carbonized and uncarbonized occurred at  $4<sup>th</sup>$  use.













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				% Absorption/recovery					
S/No.	<b>Particle</b>	<b>Contact</b>	<b>Sorbate</b>	$1st$ Use	$2nd$ Use	$3rd$ Use	$4^{\text{th}}$ Use		
	size	Time(min)							
1	$325 \mu m$	30	Crude	405 (288)			382 (216) 388 (192 305 (170)		
		60	Oil	435 (290)	398 (220)		390 (182 288 (158)		
		90		430 (294)	410 (270)		390 (184 296 (164)		
		120		450 (300)	436 (280)		398 (202 308 (172)		
$\overline{2}$	$325 \mu m$	30	<b>Diesel</b>	400 (264)			336 (220) 300 (168 288 (150)		
		60		398 (230)			330 (210) 308 (170 290 (150)		
		90		402 (220)			332 (200) 310 (170 285 (152)		
		120		418 (235)			340 (215) 310 (165 296 (156)		
3	$325 \mu m$	30	Kero-	290 (180)			280 (160) 280 (160 270 (158)		
		60	Sene	285 (175)	288 (165)		284 (160 272 (160)		
		90		292 (178)			285 (164) 286 (162 280 (160)		
		120		298 (182)			288 (166) 286 (164 290 (162)		
4	$325 \mu m$	30	petrol	280 (170)			272 (168) 260 (149 260 (150)		
		60		284 (168)			272 (170) 268 (150 265 (152)		
		90		288 (184)			275 (172) 266 (156 264 (155)		
		120		280 (186)			276 (170) 270 (158 265 (156)		
5	$625 \mu m$	30	Crude	340 (200)	310 (180)		288 (175 268 (168)		
		60	Oil	355 (202)	320 (185)		290 (180 272 (167)		
		90		365 (210)			315 (180) 292 (178 276 (170)		
		120		370 (220)			320 (190) 295 (182 278 (170)		
6	$625 \mu m$	30	<b>Diesel</b>	288 (170)			270 (168) 262 (160 258 (152)		
		60		290 (172)			272 (166) 263 (160 260 (156)		
		90		288 (170)			268 (164) 265 (162 268 (157)		
		120		295 (172)			275 (170) 270 (164 268 ((157)		
7	$625 \mu m$	30	Kero-	260 (170)			252 (150) 220 (146 208 (140)		
		60	sene	270 (175)	260 (150)		218 (146 210 (120)		
		90		286 (178)			268 (152) 225 (147 210 (122)		
		120		292 (180)			265 (156) 225 (147 215 (125)		
8	$625 \mu m$	30	petrol	220 (150)			210 (136) 202 (120 186 (110)		
		60		218 (148)			210 (138) 205 (120 188 (112)		
		90		220 (150)			212 (138) 206 (118 190 (114)		
		120	$\sim$	225 (154)			212 (135) 202 (116 192 (114)		

**Table 3a. Percentage absorption/recovery profiles of sorbates by carbonized Coco nut husk at different particle size and contact time**

















*% retention of sorbates by uncarbonized feather in parenthesis*

		% Retention						
S/No.	<b>Particle</b>	Contact	Sorbate	$1st$ Use	$2nd$ Use	$3rd$ Use	4 <sup>th</sup> Use	
	size	time (min)						
1	$325 \mu m$	30	Crude Oil	135 (108)	135 (106)	120 (109)	105 (178)	
		60		139 (134)	140 (108)	120 (108)	114 (160)	
		90		145 (138)	135 (109)	110 (109)	125 (178)	
		120		162 (145)	135 (108)	115 (107)	125 (160)	
$\overline{2}$	$325 \mu m$	30	<b>Diesel</b>	121 (112)	108 (188)	182 (182)	155 (180)	
		60		152 (120)	122 (189)	170 (185)	157 (184)	
		90		163 (115)	110 (188)	165 (190)	187 (182)	
		120		170 (120)	125 (188)	155 (188)	185 (187)	
3	$325 \mu m$	30	Kero-	124 (108)	121 (102)	149 (112)	98 (114)	
		60	Sene	124 (113)	126 (104)	150 (108)	98 (111)	
		90		124 (110)	126(102)	151 (112)	104 (114)	
		120		133 (110)	124 (110)	147 (117)	96 (117)	
4	$325 \mu m$	30	petrol	142 (102)	144 (124)	136 (114)	126 (112)	
		60		142 (102)	145 (116)	137 (112)	125 (112)	
		90		145 (105)	148 (120)	145 (115)	127 (114)	
		120		148 (104)	145 (126)	144 (115)	129 (116)	
5	$625 \mu m$	30	Crude Oil	43 (98)	122 (94)	110 (114)	94 (115)	
		60		30 (114)	125 (106)	113 (127)	100 (121)	
		90		45 (115)	126 (103)	119 (126)	100 (118)	
		120		50 (145)	127 (120)	115 (120)	102 (124)	
6	$625 \mu m$	30	<b>Diesel</b>	64 (100)	108 (100)	105 (102)	104 (100)	
		60		67 (108)	111 (103)	105 (104)	104 (105)	
		90		66 (122)	112 (102)	103 (162)	106 (98)	
		120		62 (122)	117 (120)	105 (110)	105 (105)	
7	$625 \mu m$	30	Kero-	84 (104)	84 (108)	82 (106)	102 (107)	
		60	sene	86 (112)	83 (107)	84 (108)	104 (108)	
		90		96 (107)	85 (110)	86 (108)	104 (106)	
		120		104 (110)	100 (116)	88 (110)	106 (108)	
8	$625 \mu m$	30	petrol	100(67)	102 (62)	112 (62)	116 (68)	
		60		102(63)	102 (62)	111 (62)	117 (66)	
		90		104 (66)	104 (66)	112 (66)	117(67)	
		120		109 (66)	107 (66)	113 (66)	119 (64)	

**Table 6. Percentage retention profiles of sorbates by carbonized and uncarbonized goat hair at different particle size and contact time**

*% retention of sorbates by uncarbonized goat hair in parenthesis*

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*% retention of sorbates by uncarbonized coco-nut husk in parenthesis*





*% retention of sorbates by uncarbonized corn cob in parenthesis*



# **3.2 DISCUSSION**

Results of the absorption/recovery profiles of both carbonized and uncarbonized sorbents for the sorbent-sorbate system for each particle size and contact time has been reported (Tables 1a – 4a and Tables 1b – 4b). The sorbents have very high affinity for all the hydrocarbon liquids, mopping up appreciable quantities, often more than 500% of their weight of the hydrocarbon sorbates within an average of 90mins contact time. Considering each Table (Tables 1a to 4a and 1b to 4b), at each point, viewing vertically and horizontally, it was observed that more hydrocarbons were adsorbed/absorbed as contact time increases (vertically) for each column (either 1st, 2nd, 3rd and 4th) application and decreases horizontally (across) on reuse (Table 1a – 4a). In all, percentage recovery follows the same trend (Tables 1b – 4b). Carbonized (activated) sorbents mopped up more sorbates than uncarbonized, the longer the contact time the higher the percentage absorption/recovery although minor variation exists. Smaller particle size (large surface area) absorbs the hydrocarbons more than the small surface area (large particle size). Proteinous sorbents absorbed more than cellulosic sorbents, among proteinous sorbent, feather absorbed more than goat hair as coconut husk (coir) absorbed more than corn cob when considering

cellulosic. Higher molecular weight compounds were absorbed and recovered than lower molecular weight, may be because the later are subject to high rate of evaporation. At continuous usage, that is 1st, 2nd, 3rd and 4th re-use, less sorbates were recovered (Tables 1b – 4b), this agrees with previous report where it was noted that the sorption capacities of many natural sorbents decline markedly with repeated use [20, 21, 22]. The decrease in % absorption/recovery of hydrocarbon across the Tables (horizontally) can be attributed to saturation of the pores and capillaries with the hydrocarbon liquids on re-use, this agrees with higher % retention of sorbates across the tables  $(Tables 5 - 8)$ . A number of inherent natural features of the sorbents confer on them different affinities for the hydrocarbon liquids. Feather and goat hair are keratin protein that possesses both oleophilic and aquaphobic properties for absorbing large quantities of oil through capillary action and by trapping the oil in the mat of criss-cross strands or fibers while cellulosic materials - Coconut husk (coir) and corn cob tend to be hydrophilic and would absorb water more readily than oil but do absorb oil using its fibrous cellulose/lignin strands. Also plant materials(cellulose) is made of microfibils, contains lumen and considerable amount of water in the cell walls and cell cavities (lumena),the water located inside the cell lumen is called "free water" while that inside the cell membrane is called "bound water", both are driven out by activation(heating) to create internal spaces for oil/chemical sorption [23]. Although we have stated that the effect of these natural compositions are not overriding [19], but we have shown here that they cannot be ignored, previous study has shown that cotton with enormous surface, with lengthy strings of fibers absorbed more of these hydrocarbon liquids than materials of this study [24]; having stated in a previous study that activated and natural feather absorbs more than three times all the sorbates than goat hair and coco-nut husk (coir) [19,25], that seems not to hold here (although feather still maintains highest absorption/adsorption). The disparity may be due to difference in atmospheric temperature, lowering viscosity of sorbates and increasing volatility or nature of hydrocarbons, waxy hydrocarbons may be absorbed and retained more than less waxy hydrocarbons. The present study shows that the quantity of the sorbates adsorbed depends on the nature of sorbents features such as availability of pores/voids, convolutions, lumen, lacunae, inter-fibril/fiber spaces, enhanced by carbonization/activation [19]. The mere fact that large volumes of the hydrocarbons (sorbates) can be recovered by mere hydraulic pressing, it means that the absorption/adsorption of sorbates by these sorbents cannot be attributed to any chemical interaction such as covalent or electrostatic but the binding of the hydrocarbons by the sorbents must be by physical adhesive forces such as Van der Waal, London forces and other dispersion phenomena as well as physical entanglement/occlusion [19]. Understanding the details of these weak non-bonding interactions are important in several fields of chemistry, because as inter molecular interactions control the structures of molecular clusters, crystal structures of organic molecules, binding properties of drugs, they also play a crucial role in determining the three-dimensional structures of large molecules including proteins and polymers, sorbents of present study are both protein and cellulosic polymers [26]. The high percentage retention of the hydrocarbons by the sorbents even after pressing (Tables 5 to 8) proves that the materials been considered are actually suitable for crude oil/fractional spill containment and clean-up; since a feature of good sorbent is high degree of absorption and oil retention [27], good and highly necessary when clean-up does not require recovery and disposal. The high percentage retention of the sorbates by sorbents (Tables 5, 6, 7 and 8) is a good indication of type of mechanism of absorption/adsorption involved, the first mechanism is adsorption of the oil on the surface of the sorbents and the second is absorption into spaces within individual granules or pores of fibres of sorbent (secondary absorption), these two mechanisms are effective in our study. Carbonized sorbents retained hydrocarbons because of expansion of pore size due to activation (carbonization) which led to mass loss (release of volatile and liquid products), therefore a

more complex and solid structure with a large specific surface is formed, because pores increases in number and size, new ones appear, two or more pores can merge into one with more pore surface and volume [28]. Most uncarbonized sorbents retained highest sorbates, this may be because carbonization opens up the pores (increase in the size of the pores), therefore more sorbates diffuse into the pores and effuse easily but uncarbonized sorbents has smaller size pores and capillaries which do not allow the sorbates to effuse easily. Uncarbonized protein sorbents (feather and goat hair) provides a textured surface which will increase external surface area and adsorption capacity [29]. Uncarbonized cellulose sorbents (coconut husk (coir) and corn cob) are fibrous and aggregates into a form that provides physically stable air spaces for absorption and subsequent retention of spilt oil [27]. Also, the high molecular weight compounds (long carbon chain), more viscous sorbates like crude oil and diesel are mainly adsorbed on the sorbent surface while low molecular weight compounds (kerosene and fuel) with low viscosity mainly diffuse into the pore and fibrous hollow spaces, therefore in the event of recovery by simple mechanical pressing, sorbates on the surface are easily recovered while those within internal spaces and pores are retained (Tables 5,6,7 and 8).

Though there were minor variations, it was observed that percentage absorption/recovery increases down the group (vertically) as contact time increases and decreases across (horizontally) on re-use for both particle size, activation and contact time (Tables 1a – 4a and 1b – 4b). The variation in % absorption, recovery and retention may be due to interplay of forces of absorption/adsorption and desorption due to saturation and also due to the fact that the sorbates are volatile even at ambient temperature especially the low molecular weight (less viscous) compounds, structural vibration, even atmospheric weather condition can be an important factor. Appreciable quantities of the hydrocarbons were absorbed/adsorbed and recovered even at fourth re-use and has capacity for further re-use, even up to ten times [27], the more the absorption, the more the recovery for each sorbent-sorbate system at a given contact time and particle size. A general trend can be established for the average sorption capacity of all the sorbents.

For carbonized at 325µm; feather > goat hair > coconut husk (coir) > corn cob Carbonized at 625µm; feather > goat hair > coconut husk (coir) > corn cob For Uncarbonized at 325µm; feather > goat hair > coconut husk (coir) > corn cob Uncarbonized at 65µm; feather > goat hair > coconut husk (coir) > corn cob

For all the sorbates and contact time (though minor variations exist). This study is developed for the calm waters of the river meanders, ditches, ponds and rivulets of the creeks of the Niger-Delta region of Nigeria where heavy clean-up equipment may not each. They are most suitable for containing (boom), recover and remediate oil pollution arising from minor or medium oil spill. According to Nigeria's Department of Petroleum Resource (DPR) classification, a minor spill is less than 25 barrels discharged on inland water or less than 250 barrels discharged on land, coastal or offshore water [4]. They may be used in medium or major spill after skimming to remove final traces of oil, and its use in containment may involve tier one spill line response team which applies to localized spills on land, near shore and off-shore environment. This involves spills which can be managed by the field staff with materials and equipment. The response time for such spill is around three (3) hours with crises period of around one week [4]. To solve the problem of competitive absorption of oil and water, water separators are used. In comparing the sorbents, though corn cob absorbs the least hydrocarbon, it is highly recommended in terms of cost and availability. Although this study is a laboratory one, large volume of waste sorbents will be generated after oil recovery in actual field work, leachability test was conducted using uncarbonized sorbent

with diesel regardless of the particle size, the result showed that the percentage release of the hydrocarbon into the environment is less than 3% (Fig. 1), we have determined that of crude oil in our previous study [19] and therefore they can effectively be left in an open dump to decay since they are biodegradable. A good alternative is to use them as alternative to firewood by compressing into logs under high pressure or they can be used in making particle board for furniture.

#### **4. CONCLUSION**

The following conclusions are made from the investigation; the sorbents absorb substantial quantities of the hydrocarbon liquids. The quantity absorbed depends not only on the sorbent but also upon the sorbates. Large volumes of the sorbates were recoverable by mere mechanical pressing. Two types of absorption/adsorption takes place simultaneously during the process, adsorption on the surface of the sorbents and absorption into the pores and capillaries of the sorbents. During recovery, the adsorbed sorbates on the surface are easily desorbed while the sorbates absorbed in the pores are retained. Ability to absorb and retain are features of good sorbents. Each sorbent whether carbonized or uncarbonized has a feature that makes it a good oil mop. If the sorbates are ranked, the order is generally: Crude oil > diesel > kerosene > petrol. Therefore molecular weights control their absorption and retention. Activation, particle size, contact time, hydrocarbon chain length and viscosity are major determining factors. The sorbents are biodegradable and therefore can easily be disposed. They can be used as an alternative to firewood for domestic use or for making particle board for furniture making.

## **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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