

Short Communication

Comparison of the mopping ability of chemically modified and unmodified biological wastes on crude oil and its lower fractions

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Abstract

Activated and unactivated powders of goat hair and coir (coconut husk) separated into two particle sizes were used to mop up spills of crude oil, diesel, kerosene and petrol. It was observed that the materials (sorbents) mopped up appreciable volumes of the hydrocarbon liquids (sorbates) within 90 min of contact. Activation, particle size of sorbents and molecular weight (chain length) of sorbates (hydrocarbon) are major determining factors. Carbonization and particle size enhanced the mopping ability as follows – carbonized 325 μm > uncarbonized 325 μm > carbonized 625 μm > uncarbonized 625 μm , thus activated sorbents with large surface area (small particle size) mopped more hydrocarbons than unactivated of the same particle size. The sorbates were mopped in the order – crude oil > diesel > kerosene > petrol. It was further observed that goat hair (keratin protein) with oleophilic and aquaphobic properties adsorbed more of all the hydrocarbons than coir at all sizes and treatment. Large quantities of the mopped oils were recovered by mere pressing while the waste sorbents with 0.5–2.0% leachable residual oil could be utilized as alternative to fire wood.

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1. Introduction

Nigeria economy has been described as mono economy because of its sole dependent on crude oil. The huge deposits of hydrocarbon in the Niger Delta region comprising ten states of Rivers, Bayelsa, Akwa Ibom, Abia, Imo, Edo, Ogun, Delta, Cross River, Ondo and its adjoining off shore area's, is responsible for Nigeria's ranking as the sixth largest producer of crude oil in the world (Adeyemi, 2004). The exploration and exploitation of oil involve certain alteration of the environment in conspicuously negative manner. Vegetation is cleared to make way for seismic lines, sites for drilling rigs are leveled, roads are built, drilling mud and oil may reach surface water. The inevitable effect is the millions of barrels of crude oil and

its lower fraction spills that may result from flow line/pipe-line leaks, over pressure failure/over flow process, equipment components, production operation, engineering operation, corrosion, hose failure, terminal operation and vandalization (SPDC, Nigeria 1997). The environment worst affected includes salt marshes, mangrove Swamps, coral reefs, shellfish beds, fish hatcheries and any stagnant waters without good dilute factors (SPDC, Nigeria 1997). Valuable commodities in the environment – plants and animals, harbours, beaches, marinas, etc. are devastated making them unfit for use (Institute of petroleum, 1990). Though a number of works (Fletcher, 1994; Davis, 1994) that are related to using biological means for cleaning water, testing of wood saw dusts for the cleaning of water surface from average oil spills (Hianov, 1995), the use of lignin-containing waste for cleaning water (Grigoriev, 1996), and sorption properties of lignin derivatized fibrous composites for the remediation of oil polluted receiving waters (Nenkova, 2007) have been reported. Cleaning oil

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pollution by activated and unactivated sorbents on the basis of their high sorption capacity towards oil and oil products suitable for the creeks, rivulets and interwoven water bodies of Nigeria's Niger Delta region have not been well studied. In this work, investigation was carried out on the use of two abundant biological wastes of plant and animal origin in Nigeria, as sorbents for Nigerian crude and fraction

2. Experimental

2.1. Materials

Collection of sorbents and preparation: Coir or coconut husk was collected from a local coconut Market around Awka Anambra State and goat's hair was collected from Awka main abattoir. They were thoroughly washed with soap solution, sun dried for two days before drying in an oven at 105 °C for 1 h and then ground. One-half of each ground material was carbonized at a temperature of 300 °C for 30 min, cooled and activated with IM H₂SO₄ 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 325 and 625 microns using mechanical sieve, Nylon 66 fabric whose adsorption profile had been predetermined and found to be adequate was used for construction of pillowcases/bags (2 cm × 2 cm × 1 cm) for the sorbates.

The sorbates: Crude oil assay: [C (82%), H (15%), N (0.02%), O (0.5%)]; Diesel (C₁₅–C₂₀); Kerosene (C₉–C₁₅) and Petrol (C₅–C₉) were procured from Port-Harcourt Refinery, Nigeria.

2.2. Methods

1.5 g of the sorbents (goat hair and coconut husk – both carbonized and uncarbonized) were separately encased in the pillow cases/bags, stitched and weight noted. Four pillows were introduced into the test liquid and completely immersed and withdrawn one after the other at 30, 60, 90 and 120 min intervals. Each pillow was hung in air for 5 min to drain off unabsorbed surface liquid. The quantity of liquid actually 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 3 mins for sorbate-sorbent system. Average of three operations was taken for adsorption and recovery for a particular test. From the results the percentage adsorption and recovery was calculated. The concentration of leachable oil was determined by soaking 3 g of the sorbents with crude oil for 1 h, after which the oil was squeezed out; the squeezed sorbent was soaked in 10 ml of warm xylene for 24 h to extract the residual oil from the sorbent. After filtration, the xylene layer was dried and the absorbance of the extract read on a UV–vis-

ible spectrophotometer at a wavelength of 420 nm, the result compared well with a standard. This procedure was repeated at 48, 72 and 96 h intervals.

2.3. Calculations

% leachability = 100–% retention,

$$\% \text{ retention} = \frac{A - B}{A} \times 100,$$

where *A* = initial concentration of leachable oil, *B* = concentration of leachable oil after 24, 48, 72 and 96 h.

3. Results and discussion

The results of the study reveal that the percentage adsorption profiles of the sorbents for the four liquids at 325 µm particle size were far greater than the adsorption at 625 µm particle size (Table 1). The same trend is reflected in Table 2, which show the percentage recovery of the sorbates from the carbonized and uncarbonized sorbents respectively. Comparing the data for both particle sizes, if viewed horizontally and vertically at the same time will show the superiority of adsorption of the carbonized over uncarbonized sorbents at both particle sizes. The results are very instructive; the adsorbents differently adsorb appreciable quantities of the hydrocarbon liquids, sweeping almost more than 500% of its weight, with the crude oil topping the values. Critical observance of Table 1, reveals that large quantities of the sorbates are already mopped up by the sorbents within 90 min of contact. It is also noticed that the nature of the hydrocarbon sorbates has an overriding influence on the relative affinities of sorbent-sorbate system. Thus, adsorption trend can be established as follows:

Carbonized goat hair: crude oil > diesel > kerosene > petrol.

Carbonized coir: crude oil > diesel > kerosene > petrol.

Uncarbonized goat hair: crude oil > diesel > kerosene > petrol.

Uncarbonized coir: crude oil > diesel > kerosene > petrol.

From the above, it is evident that the general affinities of these sorbents for the sorbates are in the order, crude oil > diesel > kerosene > petrol. Many materials are known to be oil absorbents or oil adsorbent, such as wood chips, activated carbon, wool, cotton balls, corn husks, duck feathers, and various synthetic and polymeric material (polypropylene, polyester, polyurethane, vinyl polymers and fabrics) and have been used to remediate oil contaminated environment (US patent 7229560B2, 2007; US patent 6978508, 2005; Nenkova, 2007).

Recently many biological materials which hitherto would have been wastes are finding useful application (Eboatu et al., 2003). Our previous paper shows that pre-

Table 1
The percentage adsorption of sorbates by carbonized and uncarbonized sorbent at different particle size and contact time

Carbonized							Uncarbonized			
Particle size	Sorbents	Time (mins)	C.O	Diesel	Kerosene	Petrol	C.O	Diesel	Kerosene	Petrol
325 μm	Goat hair	30	480	416	315	309	455	380	300	296
		60	485	437	327	320	458	384	305	312
		90	486	455	337	337	462	390	319	324
		120	510	466	367	344	471	400	330	337
	Coconut husk (coir)	30	411	395	300	230	402	340	280	220
		60	432	411	310	236	418	352	352	228
		90	440	420	314	242	420	360	360	230
		120	460	426	320	252	440	364	365	240
	Goat hair	30	355	305	268	268	300	270	260	200
		60	346	314	269	269	320	276	267	206
		90	366	330	288	288	340	286	280	210
		120	381	335	300	300	360	300	284	214
625 μm	Coconut husk (coir)	30	355	305	268	210	300	270	260	200
		60	364	315	269	218	320	276	267	206
		90	366	330	288	224	240	286	280	210
		120	381	335	300	230	360	300	284	214

Table 2
The percentage recovery of sorbates from carbonized and uncarbonized sorbents at different particle size and contact time

Carbonized							Uncarbonized			
Particle size	Sorbents	Time (min)	C.O	Diesel	Kerosene	Petrol	C.O	Diesel	Kerosene	Petrol
325 μm	Goat hair	30	321	258	209	205	312	256	203	209
		60	332	267	231	221	315	263	215	217
		90	322	276	237	229	320	271	266	228
		120	322	278	232	227	322	270	228	226
	Coconut husk (coir)	30	212	216	205	145	150	196	194	140
		60	222	226	216	149	154	199	200	143
		90	228	230	219	152	158	204	203	145
		120	232	236	222	155	162	210	208	147
	Goat hair	30	311	251	218	208	302	230	198	203
		60	313	260	223	209	307	241	211	200
		90	321	267	229	227	307	245	218	209
		120	320	274	224	229	305	251	219	207
625 μm	Coconut husk (coir)	30	170	170	156	130	150	140	150	125
		60	180	180	160	134	152	150	154	130
		90	188	188	164	138	160	158	158	134
		120	192	190	168	142	170	164	162	137

treated and natural chicken feather adsorbs more than three times all the sorbates than materials of the present study for both particle size and contact time (Nduka et al., 2007). This study shows that the quantity of the sorbate adsorbed depends on the nature of sorbents features such as availability of pores/voids, convolution, lumen, lacunae, inter-fibril/fiber spaces, specific adsorption/absorption sites (improved by carbonization) and for sorbates such factors as viscosity and molecular size (carbon chain length) are important. Since investigation were carried out at ambient temperature and pressure, it is assumed that the effect of these external influences can be considered uniform. The disparity in the amount of sorbates recovered can be explained in terms of the nature of sorbents-hair is keratin protein, so possesses both oleophilic and aquaphobic properties for absorbing large quantities of oil through capillary action while cellulosic material (coir) tend to be

hydrophilic and would absorb water more readily than oil. The effect of these natural compositions is not overriding in this present study, rather particle size (surface area) and carbonization for sorbents, viscosity and molecular weight (chain length) for sorbates are the dominant factors, this is because 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. The reason is that the hydrocarbon molecule can hardly enter into any specific interaction such as covalent or electrostatic with the sorbents. This accounts for the ease with which the absorbed hydrocarbons are desorbed, the trend observed mirrors the chain length of the hydrocarbon, those with bigger molecular chains (crude) being absorbed and retained better than the smaller molecular species (petrol), (Tables 1 and 2). This may be due to the fact that during

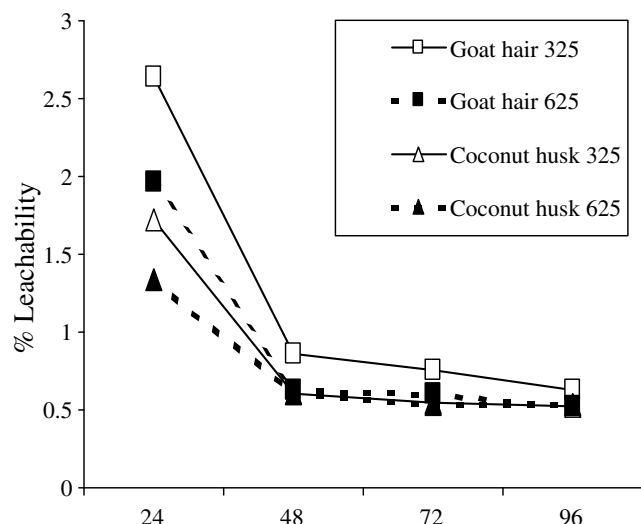


Fig. 1. The percentage leachability of goat hair and coir at 325 µm and 625 µm particle sizes of the crude oil.

drain, the smaller molecular fraction, which is of course, more loosely held, desorb more readily than long chain fractions. Also from Tables 1 and 2, it is noticed that absorption and recovery are time dependant as more hydrocarbon was absorbed and recovered from sorbent–sorbate system at 120 min contact time.

In cleaning oil spills, coir (cellulosic material) being hydrophilic is better suited on shore while the protein based (goat hair), with oleophilic and aquaphobic property will be better off shore. This will obviate the possibility of competitive or exclusive absorption of water by the sorbent, but when it does occur water separators are normally used to recover oil from oil/ water mixture. Though several materials such as hair (Urchin and Cerojano, 2006), fabrics (US patent 6978508, 2005), copolymer based materials (US patent 722560B2, 2007), has been developed to contain (boom), recover and remediate oil contamination, the environment of application is an important factor.

The present cost effective study is developed for the calm waters of the river meanders, ponds, ditches, and rivulets of creeks of Niger Delta region of Nigeria where conventional clean-up heavy equipment may not reach. To handle the problem that might arise over the disposal of large quantities of the waste sorbents after oil recovery, leachability tests were conducted using the crude oil, to determine the percentage release of the hydrocarbons into the environment when left in an open dump and impacted by rain. From the results (Fig. 1), it is obvious that between 0.5%

and 2.0% of the Crude were leached by the sorbents (i.e. more than 95% retention), it does not constitute serious environment menace considering the high volatile nature of hydrocarbons. The used sorbents could be burnt or buried since being cellulosic or protein based, they are biodegradable. A brighter application is their compression under high pressure to form logs which can serve as alternative to firewood for domestic use.

4. Conclusion

Several conclusions can be drawn from this investigation.

The sorbents absorb substantial amount of hydrocarbon liquids. The quantity absorbed depends on molecular weight of the sorbates which is in order. Crude oil > diesel > kerosene > petrol, contact time of sorbents–sorbates system, particle size and carbonization also enhance the ability of the sorbent to mop up the spilled hydrocarbon liquid. Large quantities of the hydrocarbons were recovered by mere pressing of the mopped product spill, the remainder is not easily leached when impacted by rain. They can serve as alternative to firewood.

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