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THE USE OF CORNCOBS AND WOOD DUST AS ADSORBENT IN OIL SPILL REMOVAL

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ABSTRACT
This research work is on the use of agricultural waste (corncobs and wood dust) as adsorbents for the removal of oil spills. The results have shown that ordinary corn corbs and wood dust can be used as adsorbent for crude oil spill removal. The sulphonated form of these adsorbents has the highest efficiency in terms of the adsorbility and retention capacity, due to their large porosity. Analysis of the results shows that sample of sulphonated corn cobs with particle size 1.40 mm has an appreciable retention capacity of 59% for crude oil compared to ordinary corncobs of the same particle size, which has a retention capacity of 55%. And analysis of the recovered crude oil shows negligible changes in its properties from the original crude. Hence it was concluded that corn corb and wood dust are effective adsorbent, but their sulphonated forms are more efficient in crude oil spill removal.

INTRODUCTION

Nigeria as one of the major crude oil producing nation with crude oil as its major export and foreign exchange earner, faces a constant treats of crude oil spillage. This is largely due to operational accidents, and also due to cases of sabotage, pipe corrosion, and natural causes.

Despite all measures and precautions expected to be put in place to prevent crude oil spillage there is always a dire need to clean up/remove spillage in the event of its occurrence. This is because crude oil spillage is capable of destroying aquatic life, plants, polluting land, sea and air (www.epa.gov). The added cost of crude oil spillage removal will lead to increase in the cost of production. That discourages the parties involved because of the final effects on their revenue or profit. It also required the companies and government by law and humanity to safe guard the environment and its inhabitants in the cause of their operations.

In a bid to reduce the cost of removing crude oil spill, the use of readily available agricultural waste such as rice husk and melon husk had been considered as adsorbents for removal of spilled oil, but little or nothing has been done in terms of using corncobs and wood dust (www.nalms.com). Corn is one of the most widely distributed of the world's food plants and is exceeded in acreage planted only by wheat (The New Encyclopaedia Britannica, 1982). Considering wood dust, the total yearly world production of wood is more than 2×10^9 cubic meters (in round and log form) and is steadily increasing. This is also a trend for wood products such as saw dust, ply wood etc. This brings the wood dust production to about 100 million dry tons per year (The new encyclopaedia Britannica, 1982). The production of corncobs, straw etc all together probably amounts to about 20 to 30 million tons per year in Nigeria. (www.epa.gov).

This research is aimed at using corncobs and wood dust as adsorbents for crude oil spill removal. This becomes necessary for effective control and cost reduction in the event of oil spillage removal. The aim was achieved via; Studying the quality of crude oil before and after it is recovered from the adsorbents, followed by the use of the adsorbents in their natural and sulphonated form in oil spill removal to determine their absorbility and retention capacity. to greater extent the aim was achieved.
There is no doubt that the outcome of this research work will not only make available an alternative means of removing spilled oil using agricultural waste as adsorbents but will also go a long way in saving companies and government enormous amounts of money often required to remove crude oil spillage using other mechanized methods such as oil skimmers free water knockout, and heater treater (www.nalms.com) etc.

LITERATURE REVIEW

Crude oil is a mixture of hydrocarbon and hydrocarbon derivatives ranging from methane to heavy bitumen (Perry et al, 1994). Some of its most important physical properties crude oil are; viscosity, pour point, flash point, carbon residue, salt, sediments, water, sulphur, colour contents, etc(Nelson,1999, Perry et al 1984, William & Adelf, 1991).

An accidental or intentional discharge of oil in to water or land is called oil spillage, and can be controlled by a number of ways ranging from chemical dispersion, combustion, mechanical containment and/or

adsorption (www.nalms.com). Oil spills are cause by a number of factors such as blow outs, sabotage, corrosion, equipment malfunction, natural causes such as wind, earth movement etc. Spilled oil and certain cleanup operations can threaten different types of marine habitats in different ways such as exposing the coral reefs to toxic substances within the oil, coating of prop roots of mangrove trees ,killing aquatic life, etc(www.epa.gov)

Adsorption is defined as the tendency of a solid substance to condense and retain on its surface or layer a gaseous or liquid substance (Kirk –Othmer, 1966). It depends on the attractive forces between the molecules of the substances which are in contact, exposed surface, the nature of the materials being adsorbed and temperature. Highly porous solids with very large internal area per unit volume are usually preferred because accumulation per unit area is small (Jokgense, 1979). Solids adsorbents are usually used in a granular form, varying in size from roughly 12mm in diameter to as small as 50μm. There are four types of adsorbents, which are widely used or have important potential uses on an industrial scale. These are activated carbon, activated alumina, silica gel and molecular sieves. However these are very costly and not readily available (Anderson&Rubin,1981) and can be augmented with wood dust and corn cobs, which are possible alternative source of activated carbon. Physico-chemical properties such as particle size, density and pore volume etc, provide information on the internal structure of adsorbents (George and Henry, 1977).

METHODOLOGY

A sample of crude oil was obtained along with corncobs and wood dust. The adsorption capacity of corncobs and wood dust were analysed. Several analyses which includes size analysis, uptake test, as well as, determination of retention capacity, percentage crude oil content, specific gravity, refractive index, apparent viscosity and colour were also carried out, on experimental samples. The physical and chemical properties of the recovered crude were also determined.

Source of Samples

The wood dust was obtained from a saw mill in Minna, while the corncobs were obtained from farmers in Minna area, who basically considered the corncobs as waste after they had removed the corn seedlings. The crude oil was obtained from Kaduna Refining and Petrochemical Company (KRPC).

Preparation of Samples

The agricultural waste-wood dust and corncobs were obtained and properly dried to ensure that they are moisture free. They are then crushed and sieved to maximum particle sizes of 1.40mm, 2.0mm, and 2.8mm, which are desired for optimum adsorption. The samples of wood dust and corncobs were then sulphonated using 0.5M sulphuric acid. This is done to increase the porosity of adsorbents.

EXPERIMENTAL PROCEDURE

Size analysis

After pre-treatment (drying and crushing) of the agricultural waste, the samples were sieved to obtain various particle size ranges viz (1.40mm, 2.00mm 2.80mm). The experiments were carried out starting with either the smallest particle size or the largest particle size. (Leonard and Martin; 1963)

Sulphonating the corncobs and wood dust

20ml of 0.5M sulphuric acid was added to 1.0g of the corncobs and wood dust of particle sizes of 1.40, 2.00mm, 2.8mm, and refluxed for 1hr. in a reflux condenser. (Warren and John, 1963). Leonard and Martin; 1963)

The corncobs and wood dust were then filtered, washed with water and oven dried to free it from excess acid. Afterwards the sulphonated corncobs and wood dust of different particle sizes (1.40mm, 2.0mm, 2.8mm) were added to 10ml of crude oil mixed with 2.5ml of distilled water, in a conical flask of 250ml.And stirred thoroughly with the aid of a glass rod.

Determination of Retention Capacity

10ml of crude oil was mixed with 2.5ml of distilled water. 1g. of each of the agricultural waste of particle sizes of 1.40mm 2.00mm and 2.80mm was added to the mixture in the various beakers and shaken vigorously. The adsorbent was drained off and the residue weighed. The retention capacity was determined following the method established by Warren and John, 1963.

Thus Up Take test = (weight of sorbates + Adsorbent) – Weight of residue after interacting with oil.

Determination of Percentage Crude Oil Content.

The percentage crude oil content in each of the adsorbents was determined using the relationship given below:

$$\text{Percentage crude Oil content} = \frac{Weight\ of\ residue\ or\ extracted\ oil\ (g)}{M\,\text{arg}inal\ weight\ of\ Dry\ Ground\ Solid} x \frac{100}{1}$$

(Nelson and Gates 1990)

Determination of Specific Gravity

The specific gravity and density of the crude oil were obtained with the aid of a 10ml measuring cylinder and weighing balance. The weight of the empty measuring cylinder and the weight of the 10ml measuring cylinder of 10ml crude oil was taken respectively. The density of the crude oil was found by dividing the mass of the crude oil with the volume of the crude oil, while the specific gravity was obtained by dividing the density of the crude oil with the density of water. (Perry et al-1963)

API was calculated as $$API = \frac{141.5-131.5}{\text{SP gravity}}$$

Refractive Index Determination

The refractive index was determined by placing a drop of the crude oil on a glass slab of the refractometer. The crude oil was well spread and the adjustable arms of the refractometer were adjusted to give the reading. The refractive index was taken at room temperature. (Michael and Waller 1982)

Apparent Viscosity Determination

The viscosity of the crude oil obtained was determined with the help of a "Hovillon tube". The extracted crude oil was taken off by a means of a channel shaped part of a stainless steel spatula. While the forefinger of the left hand obstructs the cover end of the tube, and the crude oil poured drop by drop in the sprayed part "A" of the tube, so that the poured volume is almost equal to the volume of the horizontal part "D" of the tube, 2 to 5 drops are required. The left forefinger was removed from the lower end of the tube, when the crude oil reaches the upper check mark part "C", a stop watch was fingered(reading to 1/60 second); and stop when the crude oil front flows through the lower check mark and the reading was taking (Nelson, 1990).

Colour Determination

The colour of the crude oil recovered from the adsorbents was determined by the use of a colorimeter. Here the cups and plungers were cleaned before and after use. The scale was adjusted to zero point then the cups with the crude oil were inserted until it touched the plunger. The instrument was adjusted for equal intensity on both sides of the cups. The intensity of a colour is proportional to the concentration of the compound. (Vanhoss, 1973)

Solvent Extraction

This involved the process of solid liquid extraction, which was done by the use of benzene as the solvent. A known quantity (7.00g) of the corncobs or wood dust (agricultural waste) with a known volume (5.5cm^3) of the crude oil was dissolved in a beaker to extract the oil (Anderson & Rubin.1981).

Adequate safety measures have to be taken to prevent the escape of benzene vapours or the inhalation of which is quite harmful.

3.0 RESULTS

The results of the various analysis conducted are shown on Table 1-3.

DISCUSSION OF RESULTS

The agricultural wastes used in the experiment were corncobs and wood dust in their ordinary and sulphonated forms. Analysis conducted on the use of these wastes in oil spill removal shows from Table 1 that ordinary corncobs and wood dust of pore sizes of 1.4, 2.0 and 2.8mm had a crude uptake of 5.5, 4.2,

3.0 for corncob and 3.9, 3.0 and 1.9 respectively for wood. While from the same table, corncob and wood dust of pore sizes of 1.4, 2.0, and 2.8mm has pore volume of 6, 4.6, and 3.5mm^3/g respectively for corn and 4.1, 3.2 and 2.2mm^3/g respectively for wood dust.

TABLE 1: TEST RESULTS ON ORDINARY WOOD DUST AND CORNCOBS.

SAMPLE	Corncobs % Pore size			Wood dust % Pore size		
	1.4	2.0	2.80	1.4	2.0	2.80
% CRUDE OIL CONTENT	55	42	30	39	30	19
PORE VOLUME (cm^3/g)	6	4.6	3.5	4.1	3.2	2.2

TABLE 2: TEST RESULTS ON SULPHONATED WOOD DUST & CORNCOBS.
BULK DENSITY OF AGRICULTURAL WASTE (CORNCOBS AND WOOD DUST
Wood dust – 0.539 kg/m^3
Corncobs – 0.483 kg/m^3

TABLE 3 PROPERTIES OF THE CRUDE OIL RECOVERED FROM THE ADSORBENTS.

PROPERTY	RECOVERED CRUDE OIL	PURE CRUDE OIL
Specific gravity. (g/ml)	0.835	0.846
Viscosity at 40^{0}C. (Centistokes)	3.0	3.4
Viscosity at 100^{0}C.(Centistokes)	25.7	26.7
Colour	Say bolt + 23	Say bolt + 26
Pour point ^{0}C	16.7	18
Refractive index	1.43	1.50

Table 2 shows that sulphonated corncob of pore sizes of 1.4, 2.0 and 2.8 had crude oil uptake of 5.9, 5.4 and 4.0 respectively while the corresponding uptake for wood dust were 4.7, 4.3 and 3.3 and respectively pore volume of 5.2, 4.2 and 5.7.

From Table 1 & 2, it was observed that as the particle size of the adsorbent decreases as the rate of adsorption increases at a constant volume of crude oil. How ever this is in agreement with what was reported by Anderson and Rubin, (1986) that the rate at which molecules strike the surface at a certain time will be exactly balanced by the rate at which molecules leave the surface. Also the adsorption of the sulphonated corncobs and wood dust was higher than that of the unsulphonated samples. This was attributed to the fact that the porosity was increased by sulphonation and more surface areas were exposed to adsorption in the sulphurnated corncobs and wood dust. Thus the sulphurnated samples of corncobs seems to have a higher tendency for the removal of oil spills than sulphurnated and unsulphurnated wood dust of the same particle size because of the increase in its porosity, which therefore increases its pore volume leading to an increase in its retention capacity.

From Table 3, analysis of recovered crude oil obtained from agricultural waste samples that was used as adsorbents in removing crude oil spills shows that the pour point of the recovered crude was 16.7^{0}C,specific gravity of 0.835, refractive index of 1.43, viscosity at 40^{0}C and 100^{0}C was 3(centiStokes) and 25.7(centiStokes) respectively while the pure crude had a pour point of 18^{0}C, refractive index of 1.5, specific gravity of 0.846g/ml,and viscosity of 3.4(centiStokes) and 26.7(centiStokes) respectively. The specific gravity of recovered oil was 1.3% less than that of pure crude oil while viscosity at 40% has higher deviation about 11% less than that of the pure crude oil.

The colour of the crude oil recovered from the sulphonated corncobs and wood dust were dirty brown,(say bolt + 23) this could be due to the reaction between the concentrated sulphuric acid and crude oil. On the other hand original crude oil was dark in colour (say bolt +26).
The quality of the recovered crude can be said to be good, since the results of the analysis carried out shows a close similarity in properties of original and recovered crude oil.

CONCLUSIONS

Analysis have shown that the ordinary corncobs and wood dust can be used as adsorbent for removal of crude oil spills, with the sulphonated form of this waste having the highest efficiency in terms of retention capacity and adsorbtivity due to increased porosity by increase in their pore size and pore volume. Analysis of the recovered crude oil shows negligible difference in properties of the recovered crude oil compared to that of original crude oil, hence it can be concluded that corncob and wood dust are very effective adsorbent for crude oil spill removal.

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