Characteristics of Some Natural Fibrous Assemblies for Efficient Oil Spill Cleanup

Sherif S. Z. Hindi
Department of Arid Land Agriculture, Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, Saudi Arabia
(shindi@kau.edu.sa)

Abstract- Oil spill cleaning is an essential head target for all environmental concerns due to its serious results in destroying marine life and vegetation. Cleaning oil spill is done by three main procedures, namely burning, isolating and skimming and collection. There is an urgent demand to improve a cheap and more efficient methods and materials for this target. Using natural fibrous resources for sorption of these contaminations satisfy most important criteria in oil collection direction. This work was done to investigate the efficiency of four natural fibrous sorbents, namely cotton fibers, seed floss of kapok (Ceiba pentandra) and milkweed or usher (Calotropis procera) and sheep fleece for sorption of three commercial petroleum oil products. Four densities of the fibrous fillers (0.2, 0.5, 0.8 and 1.1g/cm³) as well as three temperature levels were tested on three different kinds of petroleum oils, namely diesel engine oil, hydraulic oil and diesel fuel. The scanning electron microscopy showed clearly smoothness surface for both seed floss resources and the roughness of the fleece surface which has an important role in oil sorption in the later case. The higher crystallinity investigated by the wide angle-XRD of milkweed seed floss than that for kapok reflects lower porosity in the cell wall nanostructure that offers additional mechanism for kapok to hold more oil. The cotton fibers had the highest oil retention among the species studied during the temperature range. Further, oil retention of the four fibrous assemblies decreases with increases in temperature from 25° to 60°C. Higher temperatures reduce oil viscosity, making it difficult for the oil to adhere to the sorbent material. Among the species studied, oil retention of cotton fibers was the highest (about 10 g oil/g of sorbent for the assembly density of 0.2 g/cm³) and gradually decreased from kapok to milkweed and finally to sheep fleece for all the four assembly density studied. In addition, within species, the lower the assembly density the higher the oil retention obtained. Further, the assembly density of 0.8 and 1.1 g/cm³ gave very low oil retention due to the shortage occurred in the capillary bulk within them. Further, within the assembly density, there is no significant difference between the oil resources determined. The clear effect is found between the assembly densities.

Keywords- Oil retention; Fibrous assembly; Seed floss; Kapok; Milkweed; Fleece.

I. INTRODUCTION

A. Oil spill problem

Oil pollution of sea and navigable waters has attracted more public attention with the increased oil consumption. The total annual influx of petroleum hydrocarbons is about 10 million metric tons due to transportation activities. Oil pollution of the shore, in addition to the reduction of amenity, also affects marine and shore life and vegetation [1].

Crude oil released to the marine environment through accidental spillage or drainage from land causes serious damage to the environment and marine life [2]. It undergoes a wide variety of weathering processes, which include evaporation, dissolution, dispersion, photo-chemical oxidation, microbial degradation, adsorption onto suspended materials, agglomeration, etc. [3]. These physico-chemical changes enhance oil dissolution in seawater [4]. Recent oil tanker accidents in the sea are very serious, not only since they pollute the environment but also because they release heavy oil. There are three main methods of oil spill cleanup in use, namely burning, isolating and skimming, and collection [5].

The major spills of oil from oil tanks, ocean oil drilling, broken oil pipes and oil refinery operational accidents occur frequently, seriously affecting the ocean ecology and the natural environment [6] and [7]. Other minor oil spills due to ship repair and maintenance, loading and unloading oil, as well as inappropriate handling of oil sludge and tank cleaning wastewater also pose serious threat to coastal waters [8]. Also most of the dispersants are often inflammable and cause health hazards to the operators and potential damage to fowl, fish and marine mammals [2].

B. Methods of removing oil spills

The methods commonly used to remove oil involve oil booms, dispersants, skimmers, sorbents etc. The main limitations of some of these techniques are their high cost and inefficient trace level adsorption [1]. Removal of oil by sorption has been observed to be one of the most effective techniques for complete removal of spilled oil under ambient conditions [1].

Since most oil products are biodegradable, oil could be disposed of for example by composting. A biodegradable
material with excellent absorption properties would be advantageous in this respect [9].

C. Sorbent materials

One problem of the global pollution by marine oil spills is the development of a cost-effective and efficient oil recovery methods and materials [10].

There are various sorbents such as exfoliated micas, chalk powder, ekoperl, straw, sawdust, foams of polyurethane or polyether, fibers of nylon, polyethylene etc. [1]. There are many superior oil recovering materials currently on the market. However, because they are costly and cannot be used repeatedly, the emergency oil recovery operation at oil spills has its own oil-saturated wastes that require expensive post-treatment, adding tremendous cost to the oil recovery process [11]. To be considered a viable oil spill absorbent, a porous material must satisfy several criteria. The material should be hydrophobic and oleophilic, have a high rate of uptake and retention, and be able to release the absorbed oil [12], reusable, cheap and biodegradable. The hydrophobicity and oleophilicity ensure that only oil is absorbed, and not water. The high uptake capacity ensures that a large quantity of oil can be picked up relative to weight of material. Some porous polymers, such as poly (propylene) and poly (urethane) mats have been used for the absorption of spilled oil. Their maximum absorption capacity is about 10-30 g of heavy oil per 1 g of polymer [13].

Some natural sorbents prepared from cotton fiber, milkweed floss and kenaf plants were reported to have rather high sorption capacities and potential for oil recovery and sorbent [13], [14], [15] and [16]. Furthermore, Choi et al [17] studied the oil sorption capacities of various natural and man-made fibrous sorbents. The experiments were conducted in a simulated seawater bath containing oil. Natural sorbents such as milkweed, kapok, cotton, and wool showed higher sorption capacities than man-made sorbents such as polyester, polypropylene, viscose rayon, nylon 6, nylon 66, and acetate. Effects of both adsorption and absorption were seen in man-made fibers, depending on the shape and size of the sorbent.

It was reviewed by Sayed et al [18] that oil can be removed from the surface of water by contacting the oil with a non-toxic, biodegradable oil-absorbing material selected from the group consisting of pre-cooked and puffed cereals, in an amount sufficient to cause agglomeration of the oil-loaded material and formation of a buoyant semi-solid mass, and removing the buoyant semi-solid mass from the surface of the water. Such product can thereafter be compressed to recover the oil and shaped into briquettes or any other convenient form for use as fuel.

Sorbents made from structured fiber assemblies are found to be the best material to clean up the oil spill. The oil sorption and retention behaviour of sorbents are influenced by the material and structure of the sorbents and oil physical characteristics [19]. It was reviewed by Karan et al [19] that the possibility of achieving a close ecological cycle is proved by the repeated use of fibrous materials, and by the pressing into briquettes and burning of THL, wood sawdust and barks which contain oil. This demonstrates the economic benefit of developing composite sorbents on the basis of WS, THL and waste raw wool-synthetic materials [19].

D. Natural fiberous sorbents

Seed floss of kapok contains cellulose (64%), lignin (12%) and pentosan (23%) as reviewed by (Karan et al 2011). Further, they contain a waxy cutin on their surface larger than that for cotton that makes them water-repellent or so-called hydrophobic [20], [21], [22] and [23]. It was indicated that sorption capacities of the packed kapok assemblies were very much dependent on their packing densities. At 0.02g/cm², its oil sorption capacities were 36, 43 and 45g/g for diesel, ASW46 and HD40, respectively. The values decreased to 7.9, 8.1 and 8.6 g/g at 0.09 g/cm². Its sorption capacities for the three oils were significantly higher than those of PP. When the oil-saturated kapok assemblies were allowed to drain, they exhibited high oil retention ability, with less than 8% of the absorbed diesel and HD40, and 12% of the absorbed AWS46 lost even after 1h of dripping. When applied on oil-over-water baths, the kapok exhibited high selectivity for the oils over the water; almost all oils spilled could be removed with the kapok, leaving an invisible oil slick on water [24].

It was found that Calotropis procera (usher or milkweed) absorbs oil through capillary action and wool uses adsorption [17]. Furthermore, Hindi [25] that the seed floss and wood have high contents of ash (5.02% and 5.4%, respectively), lignin (20.3% and 18.5%, respectively) and low contents of total extractives (9.16% and 11.9%, respectively) and holocelluloses (61.2% and 64.2%, respectively). The chemical parameters show a decrease in the fibrous quality of the calotrope than some of other conventional natural fibers such as cotton and kapok (Ceiba pentandra). This is due to high content of ash will negatively impact the chemical recovery process and, therefore, could constitute a serious drawback [26] when the seed floss is used as a precursor for cellulose chemical industries. Accordingly, one of the good choices is using this crude material for oil spill cleaning.

Cotton is a well-known industrial textile that shows promise as an all-around effective absorbent of both oil and water. It is notable for its low density, high availability, and low cost. Cotton has a high oil up-take coefficient of up to 80 times its own weight. It is composed of mostly cellulose, which allows it to be a reusable and biodegradable material [27]. Since waxes are generally deposited in the cuticle of the cotton fiber, the mechanism of oil adsorption by interaction between waxes on fiber surface and oils is present clearly through their hydrophobic interaction and Van der Waals forces due to their similarity as hydrocarbons [28]. It was found that oil sorption of cotton fiber was controlled by adsorption on the fiber surface and capillary action through its lumen. Sorption decreased as fibrous sorbent density increased [29].

For sheep fleece, Maja, et al [30] studied the possibility of using recycled wool - based non-woven material as sorbent in an oil spill cleanup. The material sorbed higher amounts of base oil SN 150 than diesel or crude oil from the surface of demineralized or artificial seawater bath. White light scanning interferometry analysis of the fibers suggested that roughness of the wool fiber surface has an important role in oil sorption.
The laboratory experiments demonstrated that the material is reusable. Recycled wool-based non-woven material showed good sorption properties and adequate reusability, indicating that the material based on natural fibers could be viable alternative to commercially available synthetic materials that have poor biodegradability.

The goal of this work is comparing and selecting a more effective porous fibrous material in oil spill cleaning to maximize the level of absorbency to use in many applicable fields. The resultant data are expected to provide preliminary data for investigating other nonwoven assemblies with improved oil sorption properties and accelerate the cleanup process.

II. MATERIALS AND METHODS

Raw materials
Sorbent material

Four porous materials tested in this study for oil sorption capacity and studying hydrophobic-oleophilic characteristics of the natural fibers, namely seed floss of kapok (Ceiba pentandra), usher or (Calotropis procera) and cotton (Gossypium barbadense ) and sheep fleece (Figure 1). Pods of Ceiba pentandra were collected from street trees planted at the King Abdulaziz University in Jeddah. Calotropis procera (Ait). Ait. Shrubs and sheep fleece were collected randomly from Hada Al-Sham village, about 120 km far from Jeddah, Saudi Arabia. They habitat in a sandy site located at a latitude of 21° 46'.839N and a longitude of 39° 39'.911E above the sea level by 206 m. Cotton samples were chosen from imported Egyptian trade cotton. After collecting the mature pods, they air-dried in ambient temperature for 48 h and seeds were separated from floss.

Fibrous assemblies

As illustrated in Figure 2, fibrous assemblies were prepared from each of kapok, usher and cotton and sheep fleece by filling them into a circular PVC tube with 2.54 cm diameter and 2.5 cm length. Ninety holes, 1mm diameter each, on the surface were made at equidistance by thermal punching. The densities of the fibrous material were adjusted to be 0.2, 0.5, 0.8 and 1.1 g/cm³.

Tested oils

Three different kinds of oils to represents a wide variety, were tested in the application of sorbents, namely diesel engine oil (Rotella TX, SAE40), hydraulic oil and diesel fuel (Figure 3).

The physical characteristics of the diesel engine oil (10W) and hydraulic oil are presented in Table 1, while the specifications of the diesel fuel are summarized in Table 2.
TABLE I. PHYSICAL CHARACTERISTICS OF DIESEL ENGINE OIL AND HYDRAULIC OIL USED AS SORBATES

<table>
<thead>
<tr>
<th>Property</th>
<th>Diesel Engine Oil (Rotella TX, SAE40)</th>
<th>Hydraulic Oil (SAE 10W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>Standard test method</td>
<td>Value</td>
</tr>
<tr>
<td>Kinematic Viscosity at 40°C (cSt) at 100°C (cSt)</td>
<td>140</td>
<td>14.5</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>102</td>
<td>IP 226</td>
</tr>
<tr>
<td>Density (g/cm³) at 15°C</td>
<td>0.895</td>
<td>IP 365</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>216</td>
<td>IP 36</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>-9</td>
<td>IP 15</td>
</tr>
</tbody>
</table>

TABLE II. PHYSICAL CHARACTERISTICS OF SAUDI DIESEL FUEL USED AS A SORBATE

<table>
<thead>
<tr>
<th>Indices of quality</th>
<th>Gost standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Index, min.</td>
<td>45</td>
</tr>
<tr>
<td>Fractional composition</td>
<td></td>
</tr>
<tr>
<td>- 50% is distilled at 0°C not more</td>
<td>280</td>
</tr>
<tr>
<td>- 96% is distilled at 0°C not more</td>
<td>360</td>
</tr>
<tr>
<td>Kinematics viscosity at 20°C (cSt)</td>
<td>3-6</td>
</tr>
<tr>
<td>Solidification, °C, max</td>
<td>-10</td>
</tr>
<tr>
<td>Temperature of cloudiness, °C, max</td>
<td>-5</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>62</td>
</tr>
<tr>
<td>Fraction of total mass of sulfur, %, max</td>
<td>0.2</td>
</tr>
<tr>
<td>Fraction of total mass of mercaptan sulfur, %, max</td>
<td>0.01</td>
</tr>
<tr>
<td>Content of actual tar, mg/100 cm³ of fuel, max</td>
<td>25</td>
</tr>
<tr>
<td>Acidity, mg KOH/100 cm³ of fuel, max</td>
<td>5</td>
</tr>
<tr>
<td>Iodine Index, g of Iodine /100 g of fuel</td>
<td>5</td>
</tr>
<tr>
<td>Ash content, %</td>
<td>0.008</td>
</tr>
<tr>
<td>Density at 20°C (g/cm³)</td>
<td>0.840</td>
</tr>
</tbody>
</table>

**Determination of oil retention (%) of the fibrous assemblies by static sorption**

In order to investigate the influence of temperature of the oil spill environment on the sorption efficiency, the oil sorption efficiency of the proposed sorbents was studied at various controlled temperatures (25°, 40° and 60°C) after equilibrium between the tested oil and the sorbent material was reached (Figure 4).

The test cell (one liter glass beaker) was filled with 500 ml of the tested petroleum oil (Figure 4). One fibrous assembly of each sorbent material was placed hanged by a thin wire which is lowered below the top surface of the oil. A lid was placed on the cell to prevent evaporation and to protect the cell. After 15 min, the sorbent assembly with the wire were removed from the beaker and let to drain over the beaker for 5 min. The wire was placed over a clean empty weighted watch glass to catch any additional drips and immediately the saturated oil sorbent was transferred to the watch glass and the weight was recorded [31].

**Scanning Electron Microscopy (SEM)**

SEM study was used to study the surface morphology and types of anatomical features in the tangential plane samples of wood as well as the floss. The samples of each woody cubes (1cm³ each) or about ten fibrous floss were placed on the double side carbon tape on aluminium stub and dried in air. Before examination, all samples were sputtered with a 15 nm thick gold layer (JEOL JFC-1600 Auto Fine Coater) in a vacuum chamber. The specimens were examined with a SEM Quanta FEG 450, FEI, Amsterdam, Netherland. The microscope was operated at an accelerating voltage ranged from 5-20 kV.

**Figure 4. Static sorption of the three oil sorbets by the fiberous assemblies under controlled temperature**

**Figure 5. The scanning electron microscope, Quanta FEG 450, FEI used for image characterization of the fibrous sorbents.**
**X-Ray analysis of seed floss**

The wide angle X-ray diffraction spectra of the fibers were recorded on a XRD 7000 Shimadzu diffractometer (Japan) as shown in Figure 6.

![Figure 6. The X-Ray Diffractometer device (XRD 7000), Shimadzu used to study the crystallinity of the fibrous sorbents](image)

The system has a rotating anode generator with a copper target and wide angle powder goniometer. The generator was operated at 30 KV and 30 mA. All the experiments were performed in the reflection mode at a scan speed of 4°/min in steps of 0.05°. All samples were scanned in 2θ range varying from 4° to 30°. The crystallinity index of the fiber was determined by using the following equation:

\[ I_c = \left( \frac{I_{002} - I_{am}}{I_{002}} \right) \times 100 \]

where: \( I_{002} \) represents the intensity of crystalline peak arising from hemicelluloses and alpha-cellulose while \( I_{am} \) is the crystallographic plane arising from such as lignin, hemicelluloses, pectin and amorphous cellulose [32].

**III. RESULTS AND DISCUSSION**

**Characterization of fibrous material**

**Scanning electron microscopy (SEM)**

The SEM micrographs of seed floss of *Ceiba pentandra* and *Calotropis procera* and sheep fleece are presented in Figures 7, 8 and 9, respectively. The images shows clearly smoothness surface for both seed floss resources and the roughness of the fleece surface which has an important role in oil sorption.

![Figure 7. SEM micrograph of seed floss of *Ceiba pentandra*](image)

![Figure 8. SEM micrograph of seed floss of *Calotropis procera*](image)

![Figure 9. SEM micrograph of seed floss of sheep fleece](image)
X-ray diffraction characterization

X-ray diffraction (XRD) depends on creation of an interference pattern by this rays when they encounter a regularly spaced matrix such as fibers. This process has been used to determine among other things the average width of the microcrystals, the percent of crystalline regions within the fibrous material, and can be used to examine the changes in these parameters during degradation [26].

The wide angle X-ray diffraction pattern of the crude seed floss of Ceiba pentandra and Calotropis procera are shown in Figures 9 and 10. It is clear from Figure 9 that the low angle reflections at the average of 18° were found to be broad whereas the reflection (22°) is sharp and intense. These reflections are attributed to amorphous components of the calotrope seed floss (I_{am}) and crystalline components (I_{002}) crystallographic plane arising from hemicelluloses and alpha-cellulose, respectively as reviewed by Hindi [26]. When the crystalline cellulose content is high, this peak is more pronounced, and when the fabric contains large amounts of amorphous material (such as lignin, hemicelluloses, pectin and amorphous cellulose), this peak is smeared and appears with lower intensity [32], [34] and [35]. Accordingly, based on Figures 9 and 10, the crystallinity index (I_c) of seed floss of Ceiba pentandra and Calotropis procera were calculated to be 39.7% and 46.2%, respectively. This finding may explains the higher oil retention (%) of Ceiba pentandra than Calotropis procera with the different densities of the fibrous assemblies (Figure 12) as well as at the different temperatures (Figure 13). The higher crystallinity of milkweed seed floss than that for kapok reflects lower porosity in the cell wall nanostructure that offers additional mechanism for kapok to hold more oil.

Oil retention as affected by fibrous material and oil temperature

It is clear from Figure 12 that cotton fibers had the highest values of oil retention among the species studied at the three temperature levels studied. Furthermore, oil sorption capacity of the four fibrous assemblies decreases with increases in temperature from 25° to 60°C. Higher temperatures lead to a low viscosity in oil, making it difficult for the oil to adhere to the sorption material. When the temperature drops, oil viscosity increases making much more sorption of oil possible, suggesting that these sorbent material would recover more oil in colder regions than in tropical ones [33]. This is obvious from Table 1 in which kinematic viscosity values for diesel engine oil reduced from 140 cSt to 14.5 cSt when the measurements were carried at 40°C and 100°C. Similarly, this increase in oil temperature led to decrease the kinematic viscosity from 36.9 cSt to 6.4 cSt.
Oil retention as affected by fibrous material and assembly density

Examining Figure 13 revealed that, among the species studied, oil retention of cotton fibers was the highest (about 10 g oil/g of sorbent for the assembly density of 0.2 g/cm³) and gradually decreased from kapok to milkweed and finally to sheep fleece for all the four assemblies’ density studied. In addition, within species, the lower the assembly density the higher the oil retention obtained. Further, the densities of assemblies of 0.8 and 1.1 g/cm³ gave very low oil retention criteria due to the shortage occurred in the capillary bulk within them. The superior oil retention by raw cotton fibers could be explained by one or more of the four mechanisms: 1) adsorption by interaction between waxes on fiber surface and oils, 2) adsorption by physical trapping on the fiber surface through its irregular surface morphology, 3) capillary action by diffusion of oil through the cuticle to the fiber lumen and 4) capillary action through its hollow lumen from fiber ends [19]. However, these mechanisms can be used for illustration of oil retention capability of the reminder fibrous materials in a variant extent. The 2nd mechanism is clear for the sheep fleece, being the roughness of the wool fiber surface is confirmed by the SEM characterization (Figure 9) which has an important role in oil sorption. On the other hand, the fiber surface of *Ceiba pentandra* (Figure 7) and *Calotropis procera* (Figure 8) show the smoothness surface of both resources indicating that the 1st mechanism of oil sorption must be omitted for both cases. Another reason to illustrate the priority of *Ceiba pentandra* in oil retention capability comparing with those for *Calotropis procera* and sheep fleece that it possesses a high level of acetyl groups (about 13%) attached to the non-cellulosic polysaccharides as indicated by Karan et al [19]. It is well known that these acetyl groups are oleophilic groups that prefer to adhere the similar materials like oils.

**Figure 13.** Oil retention of the four fibrous assemblies made by the four different densities (g/cm³)

Oil retention as affected by assembly density and oil temperature

As shown in Figure 14 for oil retention as affected by the interaction between assembly density and oil temperature, oils retained on the assemblies were higher for the lower densities at the three oil temperature studied and vice versa. In addition, within the assembly density, the oil retention did not affected by oil temperature except for cotton fiber.

**Figure 14.** Oil retention of the four fibers densities (g/cm³) of the assemblies retained at three different temperatures

Oil retention as affected by assembly density and oil type

It is clear from Figure 15 that within the assembly density, there is no significant difference between the oil resources determined. The clear effect is found between the assembly densities.

**Figure 15.** Oil retention of the four assembly density using the three different oils

REFERENCES


