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Full Length Research Paper

Heavy oil spill cleanup using law grade raw cotton fibers: Trial for practical application

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Crude oil released to the marine environment through accidental spillage or drainage from land causes serious damage to the environment and marine life. Treatment of oil spills remains a challenge to environmental scientists and technologists. Sorption is a popular technique applied for treatment of oil spillage. In this paper, the potential of raw law value cotton fibers, to remove used oil was investigated also an attempt was made to provide an efficient, easily deployable method of cleaning up oil spills and recovering of the oil. It is important to provide a safe system for oil removal and recovery. The results presented and discussed in this work pointed out that the loose low grade cotton fibers and the pad have an excellent commercial potential as a sorbent for oil.

Key words: Used oil, sorption capacity, sorbent, low grade cotton fibers pad.

INTRODUCTION

Lubricating oil is the most valuable component in a barrel of crude oil. When it is spent (drained from the engine), it contains a variety of contaminants which are environmentally hazardous. The world environment conference held in Kyoto in 1997, confirmed the drastic need to reduce petroleum waste discharge into the environment. In fact, it was estimated that less than 45% of available waste oil was being collected world-wide in 1995. The remaining 55% was either misused or discarded by the end user in the environment. Without access to suitable treatment, used oil tends to be disposed of ways that can degrade the environment. Used oil can be illegally dumped into waterways or dumped on land or in landfills, where ground water contamination can result. On the other hand, if used lube oil is recycled properly it can help to preserve our valuable resources as well as to reduce its environmental impacts (Leask, 1998).

Whenever oil is spilled, there would be a potential to cause significant environmental impact (Bucas and Saliot, 2002). Crude oil spilt in the marine environment undergoes a wide variety of weathering processes, which include evaporation, dissolution, dispersion, photo-chemical oxidation, microbial degradation, adsorption onto suspended materials, agglomeration, etc. (Jordan and Payne, 1980). These physico-chemical changes enhance oil dissolution in seawater (Payne and Phillips, 1985).

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 (Wardley-Smith, 1983). Also most of the dispersants are often inflammable and cause health hazards to the operators and potential damage to fowl, fish and marine mammals. They can also lead to fouling of shorelines and contamination of drinking water sources (NRC, 1989).

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. Various sorbents such as exfoliated micas, chalk powder, ekoperl, straw, sawdust, foams of polyurethane or polyether, fibers of nylon, polyethylene etc. have been studied for this purpose (Wardley-Smith, 1983). Since most oil products are biodegradable, oil could be disposed of for example by composting. A biodegradable material with excellent absorption properties would be

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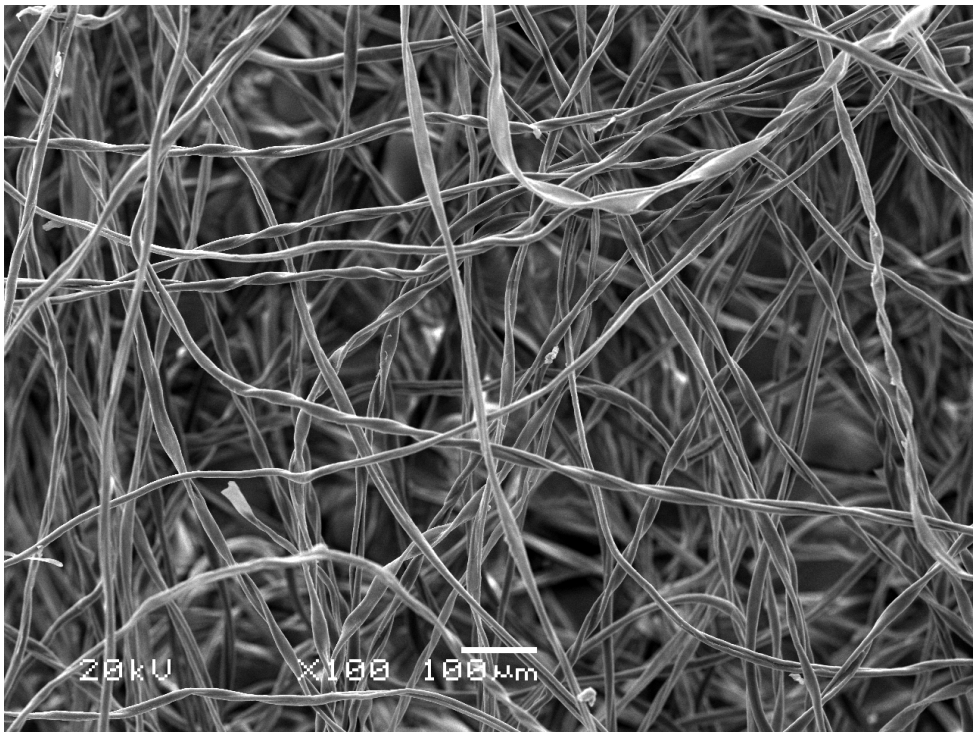

Figure 1. SEM image of raw cotton fibers.

advantageous in this respect (Suni et al., 2004).

The purpose of this work is to study the oil sorption, in aqueous medium by low quality grade cotton and not only to provide an environmentally acceptable method of cleaning up oil spills, but also to get an applicable technique which allows its recovery.

MATERIALS AND METHODS

Raw law value cotton fibers used in the study as sorbent fibers were sourced in Kafr Eldwar cotton gin, Egypt. The cotton fibers were collected in the 2006 season from the different growing regions. One type of low value cotton gin fibers (lint) by-product from the classing process was used Afriba in this study used as loose fibers and was packed in a polypropylene bag with the following specifications (Nonwoven polypropylene permeable to oil but retains the sorbent with average thickness of 65 mm, shear modulus of 6.25 N/cm^2 and modulus of elasticity (elongation of 32.2%).

Characterization of cotton samples was not carried out since the by-product cotton bales were made up of samples from different growing regions (that is, heterogeneous sample). Therefore, the cotton samples used had a variety of cotton length, uniformity, strength and colour. In addition, no cotton fibers 'conditioning' was undertaken in the experimental work. The cotton fibers were essentially used in the raw state.

Scanning electronic microscope model (SEM JEOL JSM 6360 LA" made by JEOL, Japan), was used to study the fiber surface morphology. Before examination, fiber samples were sputter coated with a thin layer of gold in a vacuum chamber (Valcineide et al., 2005). Figure 1 presented SEM micrograph of surface morphologies.

Infrared spectra were recorded on a FTIR spectrometer (JASCO FTIR-420). UV absorbance was recorded using a GBC UV. Visible spectrophotometer (GBC Cintra 5, Australia) with a 1 cm cell. The viscosity of the crude oil sample was determined by a rotary viscometer (HAAKEVT-500, Germany).The average particle size was measured with COULTER LS 230 particle size analyzer (Shashwat et al., 2006). The used oil was lubricating oil of the following specification:

Determination of dynamic oil retention and oil sorption capacity

A 500 mL sample of artificial sea water (3.5% NaCl) was placed in a 1 L glass beaker, as described in Technical Manual of the American association of textile chemists and colorists [AATCC] (Choi and Cloud, 1992). A forty mL of oil was added to the beaker. The beaker containing crude oil and artificial sea water was mounted in a shaking apparatus. The cotton (1 g) , flat cake-shaped (52 mm diameter) obtained by squeezing, was put in the system, which was shaking for 15 min at 105 cycles/ min The wet flat cake was weighed after being drained for 5 min in the sustainer. Water content of the sorbent was analyzed by the ASTM D4007-81 (ASTM, 1998a). Petroleum ether was used as the carrier solvent. The use of a flat cake shape avoids major problems of sorbent density variations (but it continues varying slightly) (Deschamps, et al., 2003) (Table 1).

Oil sorption capacity = [ST-SC-SA] / SA

Where, SA is the dry weight of the sorbent (g), ST is the total weight (g) of the oil, water and dry sorbent and SC is the weight of water (g). All tests were triplicate and the average the three runs were taken for calculation. If the value of any run deviates by more than

Table 1. Physical properties of used lube oil.

Specific gravity at 15°C	0.9057
Kinematic viscosity cSt at 40 °C (ASTM D 1298)	129.7
Kinematic viscosity cSt at 100 °C (ASTM D 445)	14.5
Water content (ASTM D 95)	2.1
Asphaltene content wt % (IP 143)	1.12

15% from the mean of three runs, then the samples were rejected and the test was repeated with three new specimens.

Evaluation of cyclic sorption/desorption characteristics

This experiment evaluated reusability of the low grade cotton fibers for cyclic oil sorption/desorption. The experiments were carried out under simulated field conditions, as described previously. The procedure was similar to that adopted by Inagaki (Inagaki et al., 2002). The oil recovery process was performed by squeezing out the absorbed oils from the test cells through a piston to determine the extent of oil sorbed by a simple mechanical device. The squeezed sorbent was used again in the sorption process. The weights of test cells and the oil squeezed out were measured in each cycle. The sorption/desorption cycle was repeated for the desired number of cycles until oil sorption capacity was less than 50% of the sorbed oil in the first cycle.

Static water test

This procedure was designed to test for water pickup under stagnant condition (hydrophobic characteristic). The test was performed at room temperature (22 to 25°C).

The test cell (one liter glass beaker) was filled with a layer of 80 mm water of salt water containing 3.5% by weight NaCl. One gram of the sorbent sample was placed in a net which is lowered into the test cell.

A lid was placed on the cell to prevent evaporation and to protect the cell. After 15 min, the sorbent with the net was removed from the beaker and let to drain over the beaker for 5 min. The net 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 (Cooper and Keller, 1992).

RESULTS AND DISCUSSION

Characterization

Electro scanning of law grade raw cotton fibers (ESEM)

Electro scanning electron microscopy has been widely used to characterize materials, particularly their morphological properties. The main focus is the role of fiber morphology on the uptake of the hydrocarbons.

Cotton adsorption mechanisms: About 1 kg of low grade cotton waste samples were fractionated into eight fractions consisting of clean lint, hulls, sticks and stems, grass, seeds, small leaf and trash (Shepherd, 1972).

About 100 g of each sample was fractionated according to the ANSI/ ASTM D 2812-95 Using Shirly analyzer (ASTM, 2006). It was found that Afriba contained 10 % impurities and 90 % fiber.

In general in raw cotton fiber, the principal component is cellulose, comprising 90 to 95% of the dry fiber weight. The remaining components are impurities such as, proteinaceous material, 0.3 to 1% waxes, 07 to 1.2% pectins and small amounts of organic acids and as producing inorganic materials (Segal, 1985). Cotton wax is an important substance that may facilitate non-polar interaction with organic compounds such as hydro-carbons.

From the SEM image in (Figure 1), an assessment of the fiber morphology can be obtained. Cotton fibers have the characteristic shape of a convoluted tube which resembles a twisted ribbon, approximately 11 µ in diameter.

FTIR spectra

The FTIR spectrum (Figure 2) of cotton fibers shows strong bands at 3352 cm^{-1} due to -OH stretching. The band at 2904 cm^{-1} corresponds to C-H asymmetric stretching of - CH2 - groups. The band at 1645 cm^{-1} is attributed to H - O- H bending and the bands at 2372 cm^{-1} are attributed to -OH stretching (Nakanishi and Solomon, 1977).

Effect of sorption time

The results of the experiments are presented in Figure 3. Figure 3 shows that the sorption capacity increases with increasing the sorption time until it reaches a maximum of 22.5 g oil/ g of fiber for used oil using cotton fibers and of 18.43 g oil/ g of fibers for used oil using cotton fibers contained in the pad at sorption time of 15 min, then these values decrease until they reach nearly constant value of sorption capacity irrespective to the soaking time due to the higher surface area of the loose fibers compared to the pad containing the low grade cotton fibers. This test was designed to study the effect of sorption time and to simulate the field conditions where a sorbent is used.

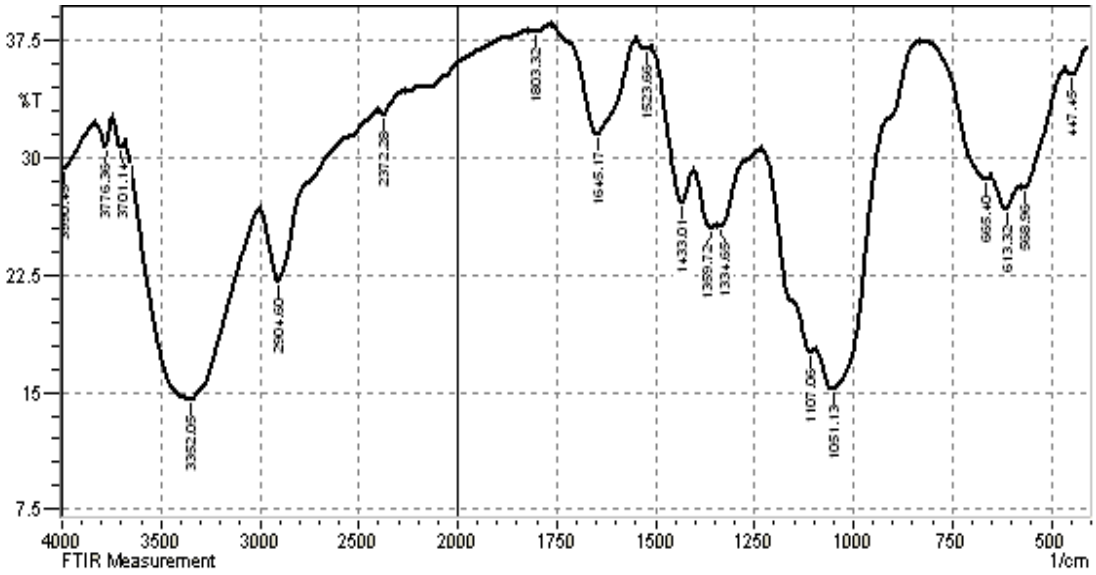

Figure 2. FITR spectra of raw cotton fibers.

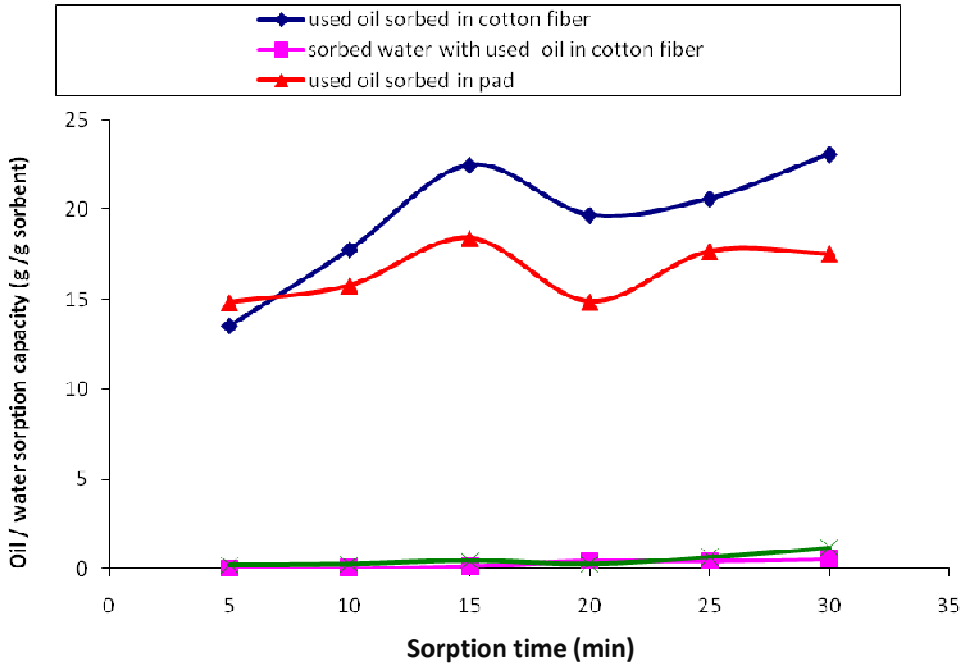

Figure 3. Effect of sorption time on the oil/water sorption capacity.

Weight of sorbent

Figure 4 shows that as the weight of the fibers increases the sorption capacity increases till it reaches a maximum value of 22.5 g oil/ g of fiber for used oil using cotton fibers and of 18.43 g oil/ g of fiber for used oil using cotton fibers contained in the pad at 1 g of cotton fibers due to big sorbent surface contacted the oil.

Effect of oil film thickness

Figure 5 shows that the sorption capacity increases with the oil film thickness until it reaches a maximum of 22.5 g oil/ g of fiber for used oil using cotton fibers and of 18.43 g oil/ g of fiber for used oil using cotton fibers contained in the pad at oil film thickness of 5 mm and that the water pick-up decreases by increasing the oil film thickness

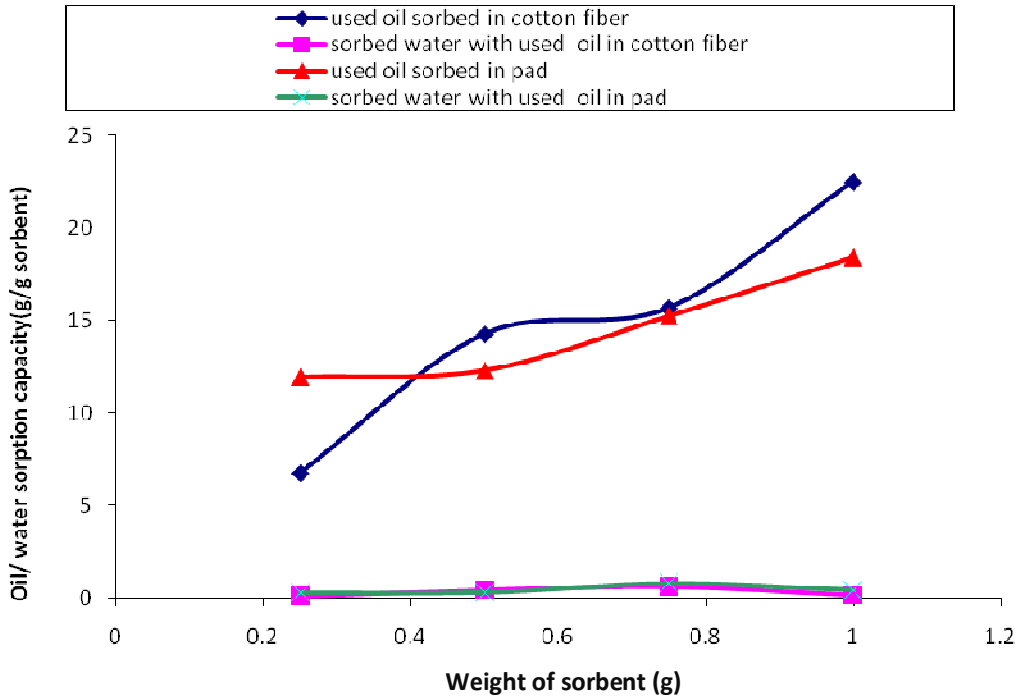

Figure 4. Effect of sorbent weight on the oil/water sorption capacity.

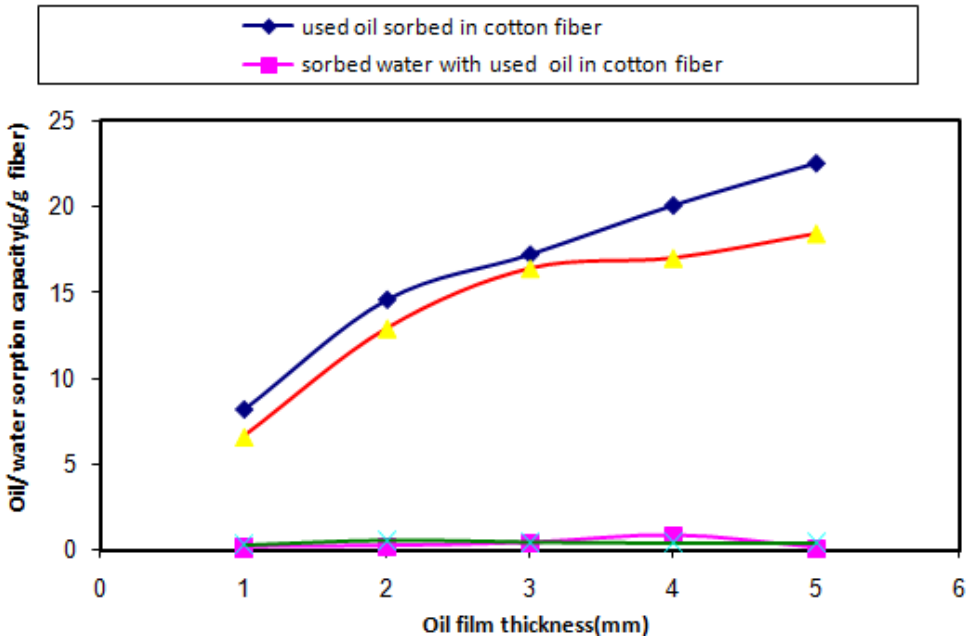

Figure 5. Effect of oil film thickness on the oil/water sorption capacity.

until it reaches the lowest value also at oil film thickness of 5 mm.

The result indicates that the sorption capacity of cotton fibers is enhanced by increase the oil film thickness till it reaches the maximum value at oil film thickness of 5 mm, the water pickup are decrease to a small value. It was shown that as the oil increases the oil contacting surface increases and the water contacting surface decreases.

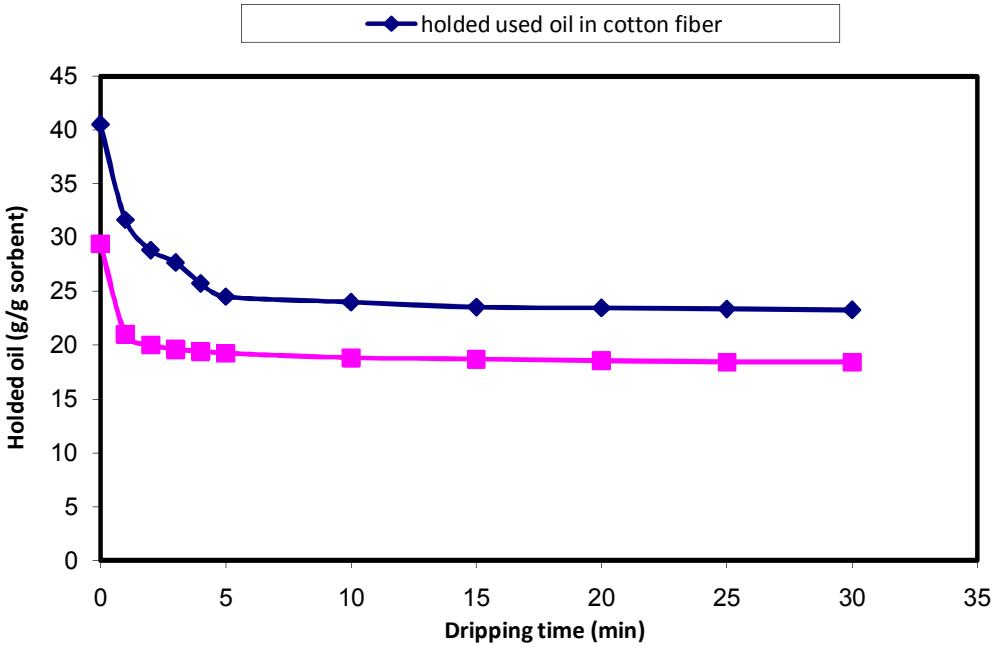

Figure 6. Effect of dripping time on the oil/water sorption capacity.

These results are in agreement with Lim and Huang (2006) and Reed et al. (1999) as they discussed that slick thickness and area are key variables in oil weathering and transport models.

Dynamic oil retention

As shown in Figure 6 in general, it shows that the dripping of oil from the surface of the cotton fibers is fast during the first 5 min. The draining process could be due to two reasons: First, it was the instantaneous dripping of oil out from external surfaces of the cotton fibers assemblies and surface of the test cells. Second, it was due to oil draining out from the extra-lumen liquids, which would continue over a longer period albeit slowly. The draining of the extra-lumen liquids occurred because the capillary pressure was insufficient to hold the weight of the oils retained in the cotton fibers. These results are in agreement with those reported by Choi et al. (1993), Wei et al. (2003) and Lim and Huang (2006) where oil retention capacity of the cotton fibers is an important parameter in evaluating the ability of sorbents to retain the absorbed oil during transfer and handling operations.

Effect of sorption temperature

The results of the experiments are presented in Figure 7. Figure 7 shows that the oil sorption capacity by cotton fibers increases with increasing the temperature until it reaches the maximum value of 22.5 g oil/ g of fiber for used oil using cotton fibers and of 18.43 g oil/ g of fiber for used oil using cotton fibers contained in the pad at 25˚C then the sorption capacity decreases again. The sorption capacity of the oil is inversely proportional to the oil viscosity and directly proportional to the capillary radius. It is also expected that a decrease in the temperature would result in a decrease in segmental mobility of the fibers, which would reduce the absorption capacity (Choi and Cloud, 1992). A compromise between these factors would occur.

These results agrees with the results obtained by Choi and Kwon (1993), whose researches were on nonwovens cotton, Johanson et al. (1973) whose reports were on unstructured fibers and Toyoda et al. (2000) whose studies were on exfoliated graphite.

Effect of reusability

The results of the experiments are presented in Figure 8. The figure illustrates that oil sorption capacity decreases during repeated use. The recovery of oil was found to decrease and the results suggest that cotton fibers can be reused for 3 and 5 times for the pad for oil spill cleanup with the aid of a suitable mechanical device which indicates that the pad enhanced the reusability. These results are in agreement Choi and Kwon (1993) and Deschamps et al. (2003). The sorbent is considered reusable if a loaded sorbent can easily compress or squeezed to its original size and shape even if there was a tendency toward decrease in sorbent efficiency with repeated sorption and desorption (Elsunni and Collier,

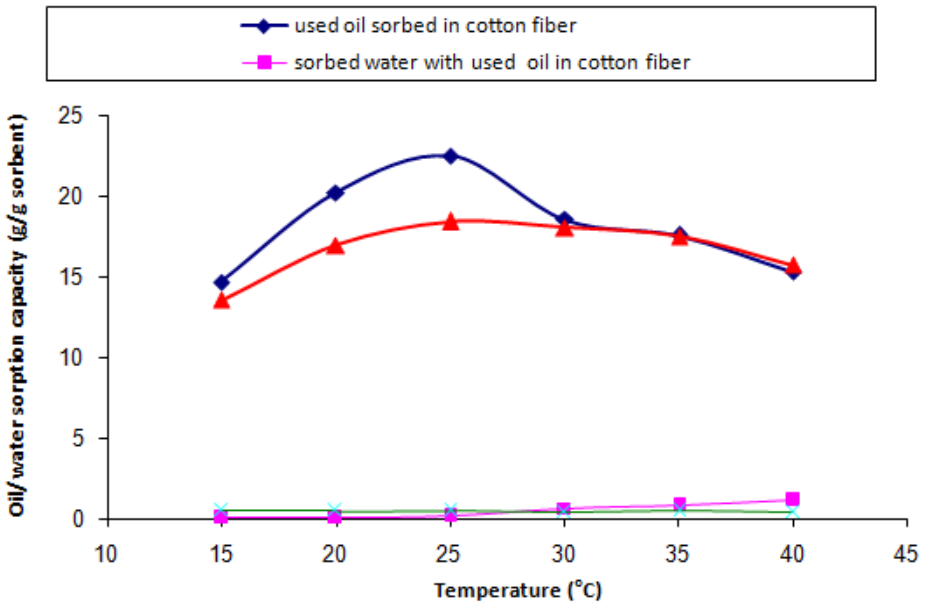

Figure 7. Effect of sorption temperature on the oil/water sorption capacity.

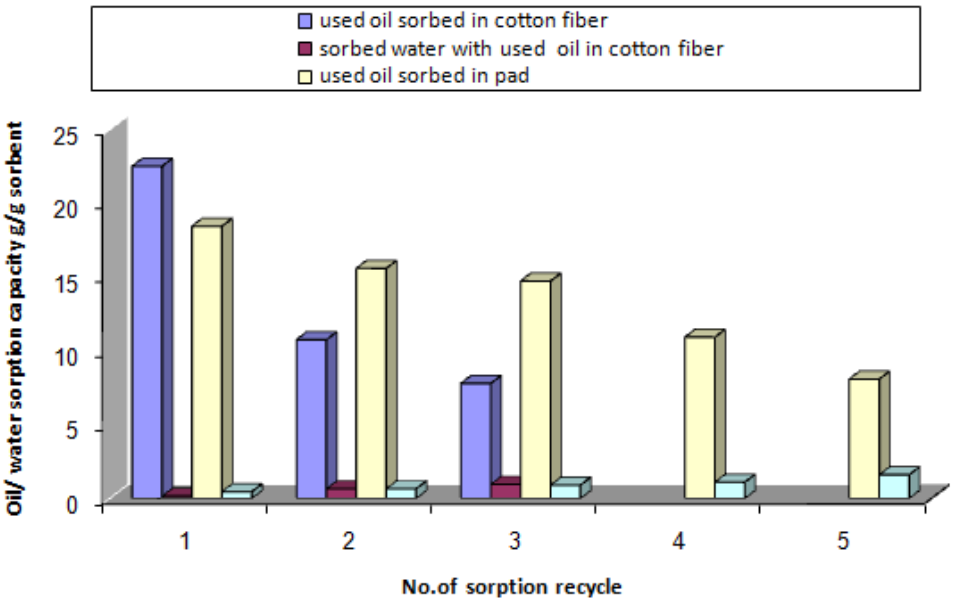

Figure 8. Effect of reusability on the oil/water sorption capacity.

1996). Although many efficient ways to recover oil from the sorbent are available, compression of the sorbent is an economical and practical method.

Comparison between the different kind of cotton wastes and commercial sorbent

Figure 9 shows comparison between the different kind of cotton wastes and commercial sorbent. The results shows that the different kind of cotton forms have higher sorption capacity of 22.5 and 18.43 g/ g fiber while the commercial sorbent which has a maximum values for used oil of 7.5 g/ g fiber.

Conclusions

In this study, an attempt was made to characterize and provide insight into the adsorption phenomena of the

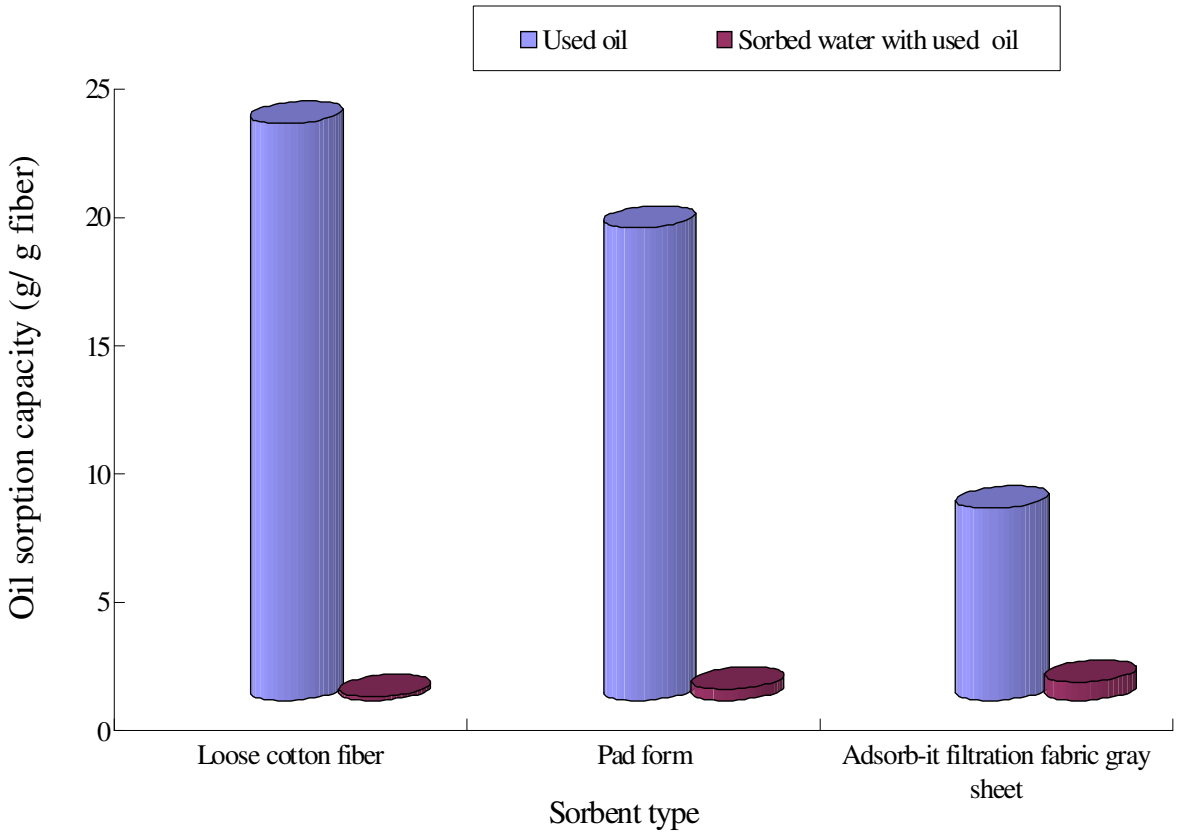

Figure 9. Comparison between the different kind of cotton wastes and commercial sorbent.

selected sorbent material using key analytical techniques. SEM was used to provide an insight into the adsorption mechanism of the cotton fiber.

The experiments carried out involved low grade cotton fibers, where their sorption capacity (g oil/ g fiber) and water pickup were compared with a pad containing low grade cotton fibers and taken as a measure to determine the potential of using low grade cotton fibers in oil-spill treatment in sea water.

The low grade cotton fibers oil sorption capacity was found to depend on sorption time and the system conditions such as oil film thickness and temperature and it was found that loose fibers has a higher sorption capacity compared to the pad containing the low grade cotton fibers due to the higher surface area of the loose fibers.

The majority of the sorbed oil was removed from the natural sorbent by a simple mechanical press suggesting that the sorbent can be used repeatedly three times in oil spill cleanup and five times for the pad.

The holding capacity of the loose fibers and the pad was found out to be good which means that the pad and loose fibers can be left without dripping the sorbed oil.

The comparison between the raw low grade cotton fibers in two forms showed that the low grade cotton fibers in loose form have the highest sorption capacity. Based on the total results obtained, the pad and loose cotton fibers have an excellent commercial potential as a sorbent for oil.

REFERENCES

American Society for testing and Materials (2006). "Book of ASTM Standers" Philadelphia, PA, pp. 722-726.

Annual Book of American Society for Testing and Materials (1998) "ASTM". D4007-81: Standard test method for water and sediment in crude oil by the centrifuge method. In: Annual Book of ASTM Standards. ASTM Committee on Standards, West Conshohocken, PA, p. 347.

Bucas G, Saliot A (2002). Sea transport of animal and vegetable oils and its environmental consequences. Mar. Pollut. Bull., 44(12):1388–1396.

Choi H, Cloud RM (1992). Natural sorbents in oil spill cleanup. Environ. Sci. Technol., 26(4): 772-776.

Choi HM, Kwon H, Moreau J (1993). Cotton nonwovens as oil spill cleanup sorbents. Textile Res. J., 63(4): 211-2118.

Choi HM, Kwon H (1993). Oil sorption behavior of various sorbents studied by sorption capacity measurement and environmental scanning electronmicroscopy. Microsc. Res. Technol., 25: 447–455.

Cooper D, Keller L (1992). Oil spill sorbent: testing protocol and certification testing program. Proceeding of the 15th AMOP Tech. Sem. Environment Canada, Edmonton, Alberta, pp. 479-497.

Deschamps G, Caruel H, Borredon ME, Bonnin C, Vignoles C (2003). Oil removal from water by sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents. Environ. Sci. Technol., 37(5): 1013-1015.

Elsunni MM, Collier JR (1996). Processing of sugar cane rind into nonwoven fibers. J. Am. Soc. Sugar Cane Technol., 16: 94-110.
Inagaki M, Kawahara A, Konno H (2002). Sorption and recovery of heavy oils using carbonized fir fibers and recycling. Carbon, 40: 105-111.
Johanson RF, Manjrekar TG, Halligan JE (1973). Removal of oil from water surface by sorption on unstructured fibers. Environ. Sci. Technol., 7(5): 430-435.
Jordan RE, Payne JR (1980). Fate and weathering of petroleum spills in the marine environment: A literature review and synopsis. Ann Arbor Sci. Publishers, Ann Arbor, MI, p. 174.
Leask D (1998). The Kyoto protocol, winners, losers, opportunities and road blocks, http://indecol.mtroyal.ab.ca/envi1214/afterkyo.
Lim T, Huang X (2006). Evaluation of Kapok (*Ceiba pentandra* (L.) Gaertn.) As a natural hollow hydrophobic-oleophilic fibrous sorbent for oil spill cleanup, Chemosphere, 66: 955-963
Nakanishi K, Solomon P (1977). Infrared Absorption Spectroscopy. Holden-Day, San Francisco, pp. 218-219.
National Research Council (NRC) (1989). Using oil spill dispersants on the sea. National Academy Press, Washington DC, pp. 265-306
Payne JR, Phillips CR (1985). Photochemistry of petroleum. Environ. Sci. Technol., 19: 569-579.
Reed M, Johansen É, Johan PB, Daling P, Levvisa A, Fiocca R, Mackay D, Richard P (1999). Modeling towards the close of the 20th Century: Overview of the State of the Art. Spill Sci. Technol. Bull., 5(1): 3-16.
Segal L, Wakelyn PJ, Lewin M, Preston J (1985). High technology fibers- Part A, Marcel Dakker Inc., New York, 3: 809.
Shashwat S, Milind V, Radha V (2006). Treatment of oil spills using organo-fly ash. Desalination, 195: 32-39.
Shashwat S, Milind V and Radha V(2006).Treatment of oil spill by sorption technique using fatty acid grafted sawdust. Chemosphere, 64:1026-1031
Shepherd JV (1972) "Agriculture handbook", Washington, DC: The Agricultural Research Service (ARS), USDA handbook no. 422.
Suni S, Kosunen AL, Hautala M, Pasila A, Romantschuk M (2004). Use of a by-product of peat excavation, cotton grass fibre, as a sorbent for oil-spills. Mar. Pollut. Bull., 49: 916-921.
Toyoda M, Kouji M, Jun-ichi A, Hidetaka K, Inagaki M (2000). Sorption and recovery of heavy oils by using exfoliated graphite-part I maximum sorption capacity. Desalination, 128: 205-211.
Valcineide OA, Thais HD, Sandro CA (2005). A comprehensive characterization of chemically treated Brazilian sponge-gourds (*Luffa cylindrica*). Polym. Test., 24: 474-482.
Wardley-Smith J (1983). The control of oil pollution. Graham and Trotman Publication, London.
Wei QF, Mather RR, Fotheringham AF, Yang RD (2003). Evaluation of nonwoven polypropylene oil sorbents in marine oil-spill recovery. Pollut. Bull., 46: 780-783.