

## Oil Spill Pollution Treatment by Sorption on Natural Cynanchum Acutum L. Plant

# <sup>a</sup>SAYED, S A; <sup>b</sup>EL SAYED, A S; S M; <sup>c</sup>ZAYED, A M

Dept. of Chemistry, Faculty of Science, Helwan University, Ain Helwan, P.No.11795, Cairo, Egypt.
 Research Center, Misr Petroleum Company, Ghamra, Cairo, Egypt.

ABSTRACT: The aim of this work is to use cheap, available, biodegradable and recyclable natural organic sorbent for oil spill clean – up. White Silky Hairs (WSH) that is collected from the smooth seeds of Cynanchum Acutum L. plant is used before treatment and after thermal and chemical treatment, to remove crude oil; 0.6 g, below which mechanical means for removing crude oil becomes less more effective, from the surface of saline water of volume 750 mL at temperature 30°C. The plant was treated mechanically by squeezing and then chemically by naphtha, a petroleum product of boiling range 30°C - 165°C, to remove sorbed crude oil from its surface for further reuse and contaminated naphtha are processed to be distilled for reuse. WSH absorbs hydrocarbons quickly and encapsulates oil on contact. WSH absorbs, on average, three times its weight. De-waxed WSH absorbs four times its weight, in case of de-waxing by n-hexane and six times its weight in case of de-waxing by methanol. Dehydrated WSH at 120°C absorbs seven times its weight. WSH absorbs televen times its weight when it is used after soaking in 10<sup>-4</sup> M dodecyl benzenesulphonic acid. WSH absorbs twenty times its weight when it is soaked in dodecyl benzenesulphonic acid and dehydrated at 120°C. Characteristics of crude oil and Cynanchum Acutum L. plant were investigated by FTIR, X – Ray Fluorescence, pour point and centrifuge instruments. Determination of amount of crude oil in saline water was done by extraction the crude oil with tricholorotrifluoroethane and measuring absorbance by Infra Red Spectrometer. @ JASEM

As the Crude oil is a very complex mixture of many different chemicals, consequently the effects of an oil spill on the marine environment is dependent on the exact nature and quantity of the oil spilled, as well as such other factors as the prevailing weather conditions and the ecological characteristics of the affected region (Doerffer, 1992; Roy, 1996). According to the complex nature of oils, they do not behave as the same in the environment. Some constituents are noted for they tendency to vaporize while others clearly prefer to bind to solids; some oil hydrocarbons extremely un-reactive while other interacts with light, so they have different toxicological effects on the aquatic life and hence on human being (Rene P. Schwarzenbach, et al., 1993).

Oil was 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 oilloaded material and formation of a buoyant semisolid 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. The method according to the invention is particularly useful for collecting and removing oil accidentally discharged into open waters by oil tanker ships and enables substantially total recovery of the oil spills (Emile Arseneault and Hervey Tremblay, 1990).

Adria Brown; and West Bloomfield, (1992), used entire dried corncobs in their nature state to remove oil spills and thereafter be used as an alternate fuel source. Corncobs were being the entire corncobs, including the zone of floral bract corncob.

John Bartha and Gyorgy Cscapo, (1992) employed the hydrocarbon wax, preferably paraffin wax, as the cleaning agent for petroleum oil spill slicks. The method include spraying the molten wax on the petroleum oil covered surface of, for example, an ocean or a coastline, allowing the wax to solidify on such surface, thereby entraining large volumes of hydrocarbon oil, then removing the solidifying wax with entrained petroleum oil from the surface. The method is repeated as often as is needed in order to fully strip the surface of the petroleum oil. The wax is recovered by heating the mixture of the solidified wax with the entrained petroleum oil therein until the wax melts, after which it is decanted from the petroleum oil and is ready for reuse in the method. Preferably, the molten wax is paraffin heated to about 75-100°C. In order to fully fluidize it so that it can be sprayed easily onto the oil-fouled surface. The wax is inert. that is, non-reactive chemically and biologically and when solidified does not stick to wild foul, fish, sea mammals, etc. Since the wax is reusable, the method is inexpensive while being efficient and fully effective.

Egyptian General Petroleum Corporation, Quality Control Dept., New Maadi, P.No. 11742, Cairo, Egypt

<sup>\*</sup> Corresponding author

Further studies were conducted by (Choi and Cloud, 1992) on milkweed and cotton fiber. When the results of these studies were compared to results gained from polypropylene (synthetic sorbent) it was shown that milkweed and cotton sorb oil more efficiently. Kenaf was discussed in the Choi and Cloud paper and was found to be comparable to polypropylene when sorbing high viscosity oil. Woody core and fiber samples of kenaf were used in this experiment. The large pieces of woody cores did not allow complete sorption to occur. Natural sorbents (milkweed, cotton and kenaf) have hydrophobic characteristics before any treatment due to the presence of surface waxes and can be used for both water and land oil spill cleanup. The natural products tested showed a much greater absorption/adsorption capacity than polypropylene (synthetic). Natural sorbents, if used effectively, can thus be more efficient than synthetic products.

A report by (Schrader,1993) compares sorption capacities of inorganic, organic, and synthetic sorbents. The inorganic sorbents had the least sorption capacity, while the synthetics had the highest. The organic sorbents, including kenaf, had moderate to high sorption capacities. The high efficiency polypropylene had the highest sorption capacity (14 to 21 grams of oil per gm of sorbent), but a lower reusability rate when compared to conventional polypropylene and wool. The cost of kenaf was low to moderate, while the synthetics had the highest costs. But no reusability tests were done on kenaf C.

(Choi and Moreau, 1993) studied the oil sorption capacities of various natural and manmade 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, viscoe rayon, nylon 6, nylon 66, and acetate. The sorption mechanisms were analyzed using a scanning electron microscope. Milkweed absorbs oil through capillary action and wool uses adsorption. Effects of both adsorption and absorption were seen in man-made fibers, depending on the shape and size of the sorbent.

Choi and Kwon, (1993), replaced the synthetic sorbents by cotton-containing nonwovens for use in oil spill cleanup. The results indicate that with light crude oil, oil sorption capacities needlepunched cotton-containing sorbents were slightly greater than those of sorbents made from 100 % polypropylene fibers. If necessary, a small polypropylene fiber could portion of into nonwovens to increase incorporated mechanical strength properties and to maintain fabric integrity. The containing sorbents were reusable after a simple mechanical compression to remove oil.

(Tiller, Zhou and Tarng, 1994) conducted experiments on kenaf bast fiber, kenaf cotton mixture, oat hulls, and a synthetic mat (New Pig Corp.) for use as oil spill sorbents. These agricultural fibers were tested for oil absorption and for use as deep-bed filters.

Glenn, et al., (1999) partially filled a plurality of water-and oil-porous sacks with a number of generally toroidal bodies of a polymer material that entraps oil and including mesh fragments scattered throughout the bodies. Each sack is sewn with a perimeter-stiffing ring, to retain a flat profile, and has netting that closes to help inhibit outflow of the oil when the sack is retrieved. When deployed from ship or by air onto a spill, the sacks spread into a pancake shape and the polymer matter forms a single layer that retains the oil. The inventive sacks will float indefinitely without releasing the oil or allowing it to emulsify, so the oil can remain in a place until collection efforts are feasible. The sacks can be burned in situ, or standard fishing boats or specialized collection boats can be used to retrieve the sacks and the collected material can be burned to capture the energy content of the oil or processed to separate the oil from the polymer. The inventive sacks can be used in conjunction with other known containment or retrieved equipment, such as booms or skimmers. the system is specifically designed for rapid deployment and efficiency in rough water.

100% natural and CANSORB, a environmentally safe absorbent, was produced by Annapolis Valley Peat Moss Co. Ltd.. CANSORB is an all organic hydrocarbon absorbent with a high humic acid content, manufactured from high quality large fiber Sphagnum Peat Moss. In the manufacturing process, the fiber is screened, processed, dehydrated and packaged in controlled conditions. The result is a product which becomes absorbing hydrocarbons, oleophilic, hydrophobic, repelling water. Due to its fiberous structure and its processing, CANSORB works to absorb hydrocarbons quickly on contact by virtue of its wicking action and encapsulates oil on This makes CANSORB ideal contact. hydrocarbon clean up both on open water and land applications. CANSORB absorbs, on average, eight times its weight. Nature has given unique properties and ingredients to the Sphagnum Peat Moss. In its natural state, the fiber contains 40%-60% water; however, the fiber has the ability to absorb 20%-40% more water and will do so on contact due to its porous nature. When CANSORB is dehydrated (activated) to 10%-12% moisture content, a wax (bitumen) is released to the surface from deep within the pores. This wax coats the outside of the fiber, resulting in the fiber resisting water within and allowing hydrocarbon absorption (Annapolis Valley Peat Moss Co. Ltd., 2000).

Hegsorb is a unique and highly effective absorbent of oil and other organic chemicals spilled in the sea or fresh water. It is made from recycled cellulosic waste, and is specially treated to absorb oil in preference to water - up to 18 times its weight. Absorbed oil is encapsulated and cannot leach out. It is supplied loose in 9 kilo bags and is easily manhandled and applied on site. It can also be used in tailor-made configurations as a filter to separate hydrocarbons from water in industrial effluents (OCBP Ltd., 2002).

Maja, et. al., 2003; study 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 demineralized or artificial seawater Superficial modification of material with the biopolymer chitosan and low - temperature air plasma led to a slight decrease of sorption capacity. Loose fibers of the same origin as non woven material have significantly higher sorption capacities than investigated non woven material. 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.

### **EXPERIMENTAL**

Gulf of Suez mixture crude oil is used for the purpose of our study since it represents about 60% of the mass production of Egyptian crude oil, which, is transferred directly to oil refining companies or for exportation along Suez Canal. It is a mixture of crude oils produced from nearly 33 fields located at the Red Sea area. Analyses figures for the tested crude oil according to the institute of petroleum (IP) test methods are listed in Table (1) (IP, 2001).

I.R spectra (FT/IR-410 Spectrometer, Jasco) of the tested petroleum crude oil was demonstrated in Table (2). Inspection of these spectra reveals the presence of the following two peaks at wave no. 2923 cm<sup>-1</sup> and 2853 cm<sup>-1</sup> represent -CH<sub>3</sub> and -CH<sub>2</sub>- stretching frequencies; two peaks at wave no 1462cm<sup>-1</sup> and 1377cm<sup>-1</sup> represent -CH<sub>3</sub> and -CH<sub>2</sub>- bending frequencies and peak at 722cm<sup>-1</sup> for aliphatic hydrocarbons of chains containing carbon atoms equal or greater than seven . These data indicate that the crude oil has a paraffinic nature (Wauquier, 1995; Silverstein, 1991).

Table 1.Physical properties of Gulf Suez mixture crude oil

Test		Test method	Results
Density at 15℃ Kg/L		IP 160	0.8544
Sediment	% mass	IP 53	NIL
Water	%Volume	IP 74	0.35
Salt	% mass	IP 77	0.004
Sulphur	% mass	IP 336	1.42
Pour point	°C	IP 15	-3
Viscosity Redweed at 37.8oC Sec.		IP 212	31
Iron	μg/ml		130
Vanadium	μg/ml	Inductive Coupled Plasma	70
Chromium	μg/ml		30

Table 2. I.R signals and assignments of the used materials.

Wave number (cm <sup>-1</sup> )	Assignment of chemical groups
3600 - 3700	Bounded Water
3400	Free Water
1000 - 1100	Ionic Phosphates
900	Ionic Carbonates
800 - 850	Silicon Carbide
700	Si or P or S
550	Conjugated Nitrite
550	Ionic Nitrite

Determination of petroleum hydrocarbons in water was done by a (American society for testing and materials ASTM D-3921, 2002) standard method. A calibration curve for determining the amount of oil on the surface of a saline water was constructing by following these steps. Prepare a stock solution of crude oil by rapidly transferring 1 ml of the crude oil to a tared 100 mL volumetric flask. Stopper flask and weigh to nearest milligram. Add tricholorotrifluoroethane solvent to dissolve and dilute to mark. Using volumetric techniques, prepare a series of standards. Select a pair of matched near-infrared silica cells. A 1-cmpath-lenghth cell is appropriate. Scan standards and samples from 3200 cm<sup>-1</sup> to 2700 cm<sup>-1</sup> with solvent in reference beam and record results on absorbance paper. Measure absorbances samples and standards by constructing a straight base line over the scan range and measuring absorbance of the maximum peak at 2930 cm<sup>-1</sup> and subtracting base line absorbance at that point. Use scans of standards to prepare a calibration curve as in Fig 1.

Procedure of determination was done by transferring the water sample to a separatory funnel coated with silicone oil, and extracting the petroleum crude oil by shaking the water sample with 30 mL tricholorotrifluoroethane solvent. Drain the solvent from bottom. Shake the water sample with another 30 mL of the solvent. Repeat with a final 30 mL of the solvent.

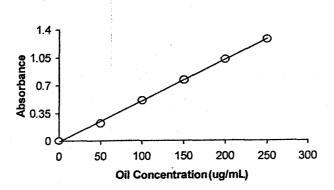


Fig. 1. Calibration curve of the tested crude oil.

Transfer extracts to 100 ml volumetric flask and dilute to the mark. Measure the absorbance. Measure the volume of extracted water. Calculate the concentration of the crude oil in water according to the following equation:

$$C = (R \times D) / V$$

Where,

C; Concentration of crude oil, mg/L.

R; Amount of crude oil in 100 mL of untreated extract, mg.

D; Dilution factor;

D = (Volume of diluted extract) / (Volume of undiluted extract).

V; Volume of extracted water.

The uptake efficiency of the petroleum crude oil on *Cynanchum* acutum L. plant was calculated according to the equation:

Uptake efficiency % = 
$$((C_0 - C_w)/C_0) \times 100$$

Where,

W<sub>0</sub> is the initial concentration and W<sub>w</sub> is the final concentration.

The adsorption isotherm in dilute solution is formulated by Freundlich as:

$$C_s = K C_w^n$$

Where  $C_s$  is the amount of oil retained by unit mass of sorbent

Cw; the amount of oil in water

K,n; constants

Another version of Freundlish is  $K_d = C_s / C_w$ 

Where the distribution ratio  $(K_d)$  describes the portioning of the oil between adsorbent and liquid phases. Strongly adsorbed oil exhibits high  $K_d$  values. The  $K_d$  is also affected by temperature,

degree of salinity, material weight, and concentration of some cations and anions that is commonly present in water (Kin H. Tan, 1998).

## CYNANCHUM ACUTUM L. PLANT

Cynanchum acutum was named by Carolus Linnaeus (1753), who named a great many plant. The author's name is usually abbreviated. Linnaeus is abbreviated as simply "L." as he is considered the father of botanical nomenclature. So, finally the plant is written as Cynanchum acutum L. and its morphological parts are illustrated in Fig 2 (MBG, 2003). The plant is a perennial climber of mature height three meters with white flowers of mm and smoothed seed capsules with a terminal tuff of long white silky hairs as shown in Fig 3C and its leaves and stems contain rubber as in Fig 3B. As shown in Fig 3A, it is easily grown in ordinary garden soil as a climber plant, supporting itself by twining over other plants (Thomas and Allen, 1997). Also, taxonomic hierarchy of Cynanchum acutum L. was demonstrated in Table 2. The physico-chemical properties of the long white silky hairs of the plant seeds (WSH Sorbent) is demonstrated in Table 3. Globally, Cynanchum acutum L. grows in North Africa, Australia, South Europe, and Southern West Asia on coastal and salt soils, hedges, mountain slopes and river banks. Locally, here in Egypt it grows in the Nile region including the Delta, Valley and Fayum, the oases of the western desert including Wadi Natrun, Siwa, Farafra, Bahariya, Kharga, Dakhla, Kurkur, Dungul and Uweinat, and the Mediterranean coastal strip from the boarder with Libya near El Sollum to Port (Loutfy Boulos, 1995). This sweet-scented climber (family Asclepiadaceae) is quite toxic and not used medicinally (FDA, 1996), although it did long ago feature in the French pharmaceutical Codex (Garnier, et al., 1961) as a purgative. The latex of the plant is still used in Tunisian folk medicine as external application for skin and eye problems (Boukef, 1986).

ASCLEPIADACEAE

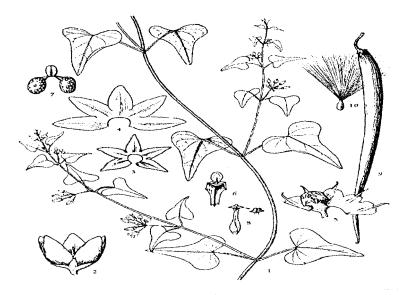


Figure (2): Parts of the plant Cynanchum acutum Linnaeus;

- 2) Flower
- Opened calyx showing glands
   Stamen adaxial view
- 1) Flowering branch
  lands 4) Opened corolla
   7) Pollinarium
   10) Seed

- 5) Column and opened corona 8) Pistil
- 9) Follicle

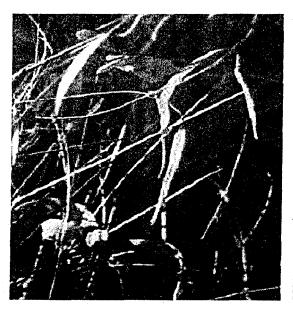


Fig. 3 A

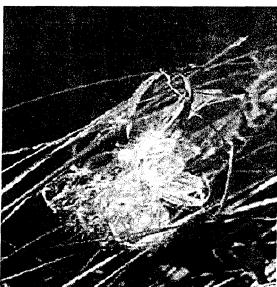


Fig. 3 B

Fig 3A. The plant Cynanchum acutum Linnaeus; the shrub on a hedge

Fig 3B. The plant Cynanchum acutum Linnaeus; a terminal tuff of long white silky hairs.

Table 3. Taxonomic hierarchy for Cynanchum acutum L.

Kingdom	Plantae -Plants	
Subkingdom	Tracheobiota - Vascular Plants	
Super Division	Spermatophyta – seed plants	
Division	Magnoliophyta - Flowering Plants	
Class	Magnoliopsida Dicotyledons	
Subclass	Asteridae	
Order	Gentianales	
Family	Asclepiadaceae - Milkweed Family	
Genus	Cynanchum L. swallow-wort	

### RESULTS AND DISCUSSION

A terminal tuff of long white silky hairs (WSH), as shown in Fig.3B, was collected manually from the smooth seeds of Cynanchum acutum L. plant. The uptake efficiency percent of WSH to remove oil spills from the surface of saline water was studied at various condition parameters of degree of expressed as sodium chloride salinity, concentration. contacting time. permanent hardness, expressed as calcium and magnesium chloride and temporary hardness expressed as sodium bicarbonate and carbonate. Also, it was studied after drying at different temperature and after de-waxing in n-hexane, methanol and soaking in dodecylsulphonic acid successfully.

The effect of the degree of salinity, expressed in NaCl concentration units, on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of different concentrations of sodium chloride, expressed in molarity of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with 0.15 g of WSH weight for one minute contacting time. Fig. 4.; shows that as the concentration of sodium chloride increases, the uptake efficiency percent of WSH increases till it reaches a value of 70% at which the maximum concentration was 5 M. this is due to the increase of density of the saline medium, which increase the buoyancy of WHS on the surface of water and hence its contacting with the oil spill. Density was measured by ASTM D-1429, 2002 test method and it was found nearly to one for pure water and 1.204 for saline water of 5 M NaCl.

The effect of the contacting time, expressed in minutes, on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M NaCl of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with 0.15 g of WSH for different contacting times. Fig. 5.; shows that uptake efficiency percent of WSH increases as contacting time increases till it reaches a maximum value 70% at one minute.

Table 4. Physico-Chemical properties of WSH sorbent (Mabberely, 1993; USDA, 2003). (ASTM, 2002; Conard, 1944).

Test (% mass)	Test method	Results
Wax content by using hexane	ASTM D- 4920/96	4.38
Wax content by using methanol	1-	4.995
Water content at 50°C	Ind. Eng	4.46
Water content at 90°C	Chem. Anal.	6.28
Water content at 105°C		7.98
Water content at 120°C		10.21

The effect of the temperature, expressed in degree C, on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M NaCl of volume 750 mL that contains 0.6 g crude oil on its surface with 0.3 g of WSH at different temperatures. Fig. 6.; shows that WSH tends not to retain oil spills efficiently above 50°C, at which the oil spill tends to be spread over area and to disperse with the saline water.

The effect of WSH weight, expressed in grams, on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M NaCl of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with different weights of WSH for one minute. Fig. 7.; shows that as WSH weight increases, the uptake efficient percent increases till it reaches maximum value of 100% at WSH weight of 0.30 g. this due to the surface area increase as the weight increases.

The effect of permanent hardening calcium and magnesium cations, expressed as calcium and magnesium chloride and temporary hardening bicarbonate and carbonate anions, expressed as sodium bicarbonate and carbonate on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M NaCl of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with 0.15 g WSH for one minute. Fig. 8.; show that as the concentration of MgCl<sub>2</sub>, CaCl<sub>2</sub>, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> increases, the uptake efficiency percent increases. This due to as the concentrations of these materials increase, the oil spill tends to be more viscous and not spread over a large area that enhance the contact between the oil spill and WSH (Singh and Pandey, 1991;

Distribution ratio (Kd) of the amount of oil retained by unit mass of WSH to the amount of oil in water was studied by plotting Cs versus Cw at optimum conditions of contacting time one minute, temperature 30°C, 5 M NaCl and WSH weight as in Fig. 9., where, the slope of the resulting straight line is Kd. It is clear from the Fig.9. that Kd is 3.28; it means that WSH can sorb oil up to three times its weight.

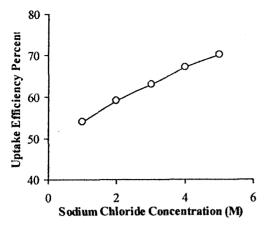


Fig.4. Effect of NaCl concentration on the uptake efficiency percent of WSH sorbent at sorbing weight 0.15 g, 30℃, crude oil content 0.6 g and contacting time one minute.

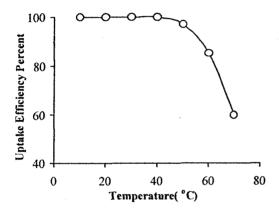


Fig.6. Effect of temperature concentration on the uptake efficiency percent of WSH sorbent at WSH weight 0.30 g, NaCl concentration of 5 M, crude oil content 0.6 g and contacting time one minute.

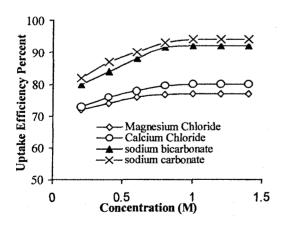


Fig.8. Effect of magnesium and calcium chloride and sodium bicarbonate and carbonate on the uptake efficiency percent of WSH sorbent at WSH weight 0.30 g, NaCl concentration of 5 M, crude oil content 0.6 g, 30°C and contacting time one minute.

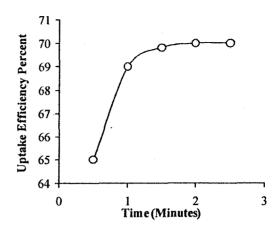


Fig.5. Effect of sorbing time on the uptake efficiency percent of WSH sorbent at NaCl concentration of 5 M, 30°C, crude oil content 0.6 g and WSH weight 0.15 g.

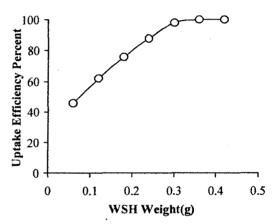


Fig.7. Effect of sorbing weight on the uptake efficiency percent of WSH sorbent at NaCl concentration of 5 M, crude oil content 0.6 g, 30°C and contacting time one minute.

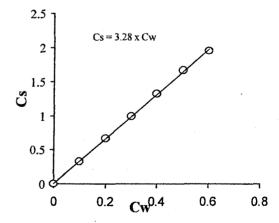


Fig.9. Distribution ratio (Kd) between WSH sorbed phase and the saline water at NaCl concentration of 5 M, crude oil content 0.6 g, WSH weight 0.15 g, 30°C and contacting time one minute.

As haven discussed before the natural WSH material that, has been collected from Cynanchum acutum L., have hydrophobic characteristics before any treatment due to the presence of surface waxes (Choi and Cloud, 1992). So, it is used for oil spill The effect of dehydration of WSH on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with different weights of dehydrated WSH for one minute. Fig. 10.; shows that as the temperature of dehydration increases the uptake efficiency, percent increases. This because When WSH is dehydrated by drying at different temperatures, a wax that is deep within the pores is released to the surface and coats the outside of WSH fiber, resulting in the fiber resisting water within and allowing hydrocarbon absorption (Annapolis Valley Peat Moss Co., 2000).

Distribution ratio (Kd) of the amount of oil retained by unit mass of dehydrated WSH to the amount of oil in water was studied by plotting Cs versus Cw at optimum conditions of contacting time one minute, temperature 30°C, sodium chloride concentration 5 M and dehydrated WSH weight as in Fig. 11., where, the slope of the resulting straight line is Kd. It is clear from Fig.11. that Kd is 6.66; it means that WSH can sorb oil up to seven times its weight.

The effect of de-waxing of WSH with nhexane (a non polar solvent) and methanol (a polar solvent) on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with different weights of de-waxed WSH for one minute. Fig. 12.; shows that uptake efficiency percent in case of de-waxing WSH with methanol is greater than in case of n-hexane because methanol remove waxes more efficient than n-hexane as demonstrated in Table.4.; as the waxes were removed, uptake efficient increases because the outer surface of WSH fiber becomes of much more surface area for adsorption as well as, absorption by capillary attraction forces.

Distribution ratio (Kd) of the amount of oil retained by unit mass of de-waxed WSH to the amount of oil in water was studied by plotting Cs versus Cw at optimum conditions of contacting time one minute, temperature 30°C, sodium chloride concentration 5 M and de-waxed WSH weight as in Fig. 13., where, the slope of the resulting straight line is Kd. It is clear from Fig.13. that Kd is 4.16 in case of n-hexane and 5.55 in case of methanol; it means that WSH can sorb oil up to four times its weight incase of n-hexane and 6 times its weight in case of methanol.

The effect of treating of WSH with dodecyl benzenesulphonate, where WSH were soaked in 10<sup>-4</sup> M dodecyl benzenesulphonate for 24 hours, on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with different weights of treated WSH with dodecyl benzenesulphonate for one minute. Fig. 14.; shows that uptake efficiency percent increases as the WSH weight increases till it reaches maximum value of about 100% at dodecyl benzenesulphonate WSH weight of about 0.09 g.

Distribution ratio (Kd) of the amount of oil retained unit mass of dodecyl by benzenesulphonate treated WSH to the amount of oil in water was studied by plotting Cs versus Cw at optimum conditions of contacting time one minute, temperature 30°C, sodium chloride concentration 5 M and dehydrated WSH weight as in Fig. 15., where, the slope of the resulting straight line is Kd. It is clear from Fig.15. that Kd is 11.1; it means that WSH can sorb oil up to eleven times its weight.

The effect of dehydrating WSH at 120°C followed by treating of WSH with dodecyl benzenesulphonate, where WSH were soaked in 10<sup>-4</sup> M dodecyl benzenesulphonate for 24 hours, followed by drying in open air for 24 hours on sorption of oil spill from the surface of a saline water was studied by contacting a saline water of 5 M sodium chloride of temperature 30°C and volume 750 mL that contains 0.6 g crude oil on its surface with different weights of treated WSH for one minute. Fig. 16.; shows that uptake efficiency percent increases as the treated WSH weight increases till it reaches maximum value of about 100% at treated WSH weight of about 0.06 g.

Distribution ratio (Kd) of the amount of oil retained by unit mass of dehydrating and dodecyl benzenesulphonate treated WSH to the amount of oil in water was studied by plotting Cs versus Cw at optimum conditions of contacting time one minute, temperature 30°C, sodium chloride concentration 5 M and dehydrated WSH weight as in Fig. 17., where, the slope of the resulting straight line is Kd. It is clear from Fig.17. that Kd is 20.00; it means that WSH can sorb oil up to twenty times its weight.

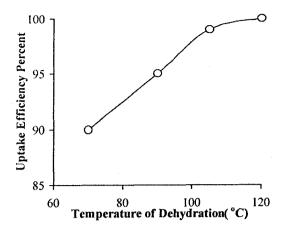


Fig.10. Effect of temperature of dehydration of WSH on the uptake efficiency percent of WSH sorbent at NaCl concentration of 5 M, crude oil content 0.6 g, WSH weight 0.15 g, 30°C and contacting time one minute.

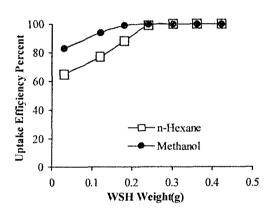
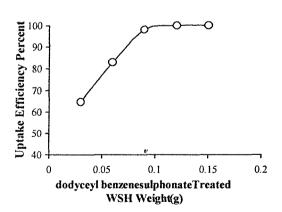
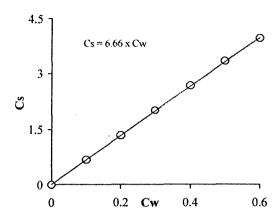


Fig.12. Effect of dewaxed WSH with n-hexane or methanol on the uptake efficiency percent of WSH sorbent at NaCl concentration of 5 M, crude oil content 0.6 g, 30°C and contacting time one minute.



**Fig.14.** Effect of treating WSH with dodecyl benzenesulphonate on the uptake efficiency percent of WSH sorbent at NaCl concentration of 5 M, crude oil content 0.6 g, 30°C and contacting time one minute.



**Fig.11.** Distribution ratio (Kd) between dehydrated WSH at 120°C sorbed phase and the saline water at NaCl concentration of 5 M, crude oil content 0.6 g, WSH weight 0.15 g, 30°C and contacting time one minute.

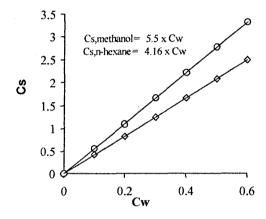
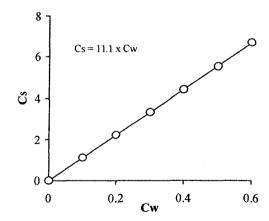


Fig.13. Distribution ratio (Kd) between treated WSH with n-hexane or methanol sorbed phase and the saline water at NaCl concentration of 5 M, crude oil content 0.6 g, 30°C and contacting time one minute.



**Fig.15.** Distribution ratio (Kd) between dodecyl benzenesulphonate treated WSH sorbed phase and the saline water at NaCl concentration of 5 M, crude oil content 0.6 g, 30°C and contacting time one minute.

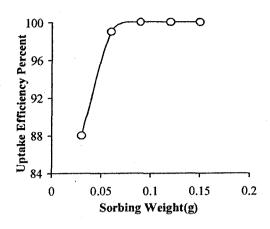


Fig.16. effect of dehydrating WSH at 120°C followed by treating of WSH with dodecyl benzenesulphonate, followed by drying in open air on the uptake efficiency percent of WSH sorbent at NaCl concentration of 5 M, crude oil content 0.6 g, 30°C and contacting time one minute.

## REFERENCES

Adria Brown and West Bloomfield, "Methods for removing oil spills using a natural, recyclable absorbent", U.S. Patent 5,160,629, 1992

American Society for Testing and Materials, ASTM D-1429, 2002 .

American Society for Testing and Materials, ASTM D-3921, 2002.

American Society for Testing and Materials, ASTM D-4920, 2002 .

Annapolis Valley Peat Moss Co. Ltd., "Cansorb product", Berwick, Nova Scotia, Canada, 2001.

Boukef, M.K., "Médicine traditionnelle ét pharmacopée – Les plants dans la medicine traditionelle Tunisienne", ACCT, P. 350, 1986.

Choi, H., and Cloud, R.M., "Natural sorbents in oil spill cleanup", Environmental Science and Technology, Vol. 26, No. 4, pp.772 – 776, 1992.

Choi, H., and Moreau, J.P., "Oil spill sorption behavior of various sorbents studied by sorption capacity measurement and environmental scanning microscope", Microscopy Research and Technique, Vol. 25, No. 5, pp. 447–455, 1993.

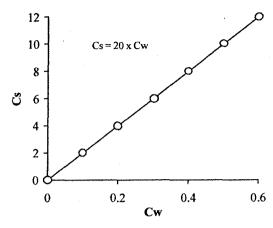


Fig.17. Distribution ratio (Kd) between dehydrated, dodyceyl benzenesulphonate treated WSH sorbed phase and the saline water at NaCl concentration of 5 M, crude oil content 0.6 g, 30°C and contacting time one minute.

Choi, H., Kown, H., and Moreau, J.P., "cotton non-wovens as oil spill clean up sorbents", Textile Research Journal, Vol. 63, No. 4, pp.211–218, 1993.

Conard, C.M., "Determination of wax in cotton fiber: A new alcohol extraction method", Industrial Engineering Chemical Analysis, Vol. 16, pp. 245, 1944.

Doerffer, J.W., "Oil spill response in the marine environment", Pergamon Press, Oxford, pp. 391, 1992.

Emile Arseneault and Hervey Tremblay, "Use of pre-cooked and puffed cereals as oil spill sorbents", U.S. Patent 4,969,774, 1990.

Environmental Protection Agency (EPA), "Understanding oil spills and oil spill response", Publication 2000 – 963401, U.S. EPA, Office of Solid Waste and Emergency Response, Dec. 1999.

FDA, U.S. Food and Drug Administration (FDA), "Poisonous plant list", Center of Food Safety and Applied Nutrition, Office of Plant and Diary Foods and Beverages, 1996.

Garnier, G.; Bézanger – Beauquesne, L., and Debraux, G., "Medical resources of French flora", Vol. 1, P. 1511, Vigot Fréres, Paris, France, 1961.

- Glenn R. Rink; Robert L. Rosania; David R. Smith; Thomass C. Johnson; Jan R. Hegeman and Peter A. Allen, "Methods for ameliorating oil spills in marine and inland waters", U.S. Patent 5, 863, 440, 1999.
- Institute of Petroleum (IP), 2001 Test Methods, Vol. 1,2.
- John Bartha and Gyorgy Csapo, "Method of cleaning up petroleum oil soils", U.S. Patent 5, 112, 495, 1992.
- Loutfy Boulos, "Flora of Egypt", Al Hadara Publishing, 1<sup>st</sup> Edition, Cairo, Egypt, 1995.
- Mabberley, D.J., "The plant book", Cambridge University Press, U.K., 1993.
- Missouri Botanical Garden (MBG) Tropicos, Nomenclature Data Base, Flora of China Illustrations, Vol. 16, Figure 182, 2003.
- Oil Cleaning Bio-Products Ltd (OCBP), "Petroleum absorbent for oil spills on water", OCBP, Hertfordshire, U.K, 2002
- Maja, M.R.; Dragen, M.J.; Petar, M.J.; Zoran, P.L., and Helga, T.F., "Recycled wool based non woven material as an oil sorbent", Environmental Science and Technology, Vol. 37, No. 5, pp. 1008 1012, 2003.
- Rene P. Schwarzenbach, Philip M. Gschwnd, Dieter M. Imbden, "Environmental organic chemistry", John Wiley and Sons, Inc., U.S.A., 1993.
- Roy M. Harrison, "Pollution causes, effects and control", Third Edition, Royal Society of Chemistry, U.K., 1996.

- Schrader, E.L., "A practical composition of organic, synthetic and inorganic sorbents", Paper Presented at the Clean Gulf 93 and the American Chemical Society Conference: Emerging Technology in Hazardous Waste Managements, pp.17, 1993.
- Silverstein, R.M.; Clayton Bassler, G. and Terence C. Morrill, "Spectrometric identification of organic compounds", Jone Wiley & Sons, London, Inc., 1991.
- Singh, B.P.; Pandey, B.P., "Physical characteristics of natural films formed at a crude oil water interfaces", Indian Journal of Technology, Vol. 29, pp. 443 447, 1991
- Thomas, R.D. and Allen, C.M., Atlas of the Vascular Flora of Louisiana, Volumes 1 3, Louisiana Department of Wildlife and Fisheries, Baton Rouge, U.S.A., 1997.
- Tiller, F.M.; Zhou, F., and Tarng, D., "Agriculture fibers as aids in separation: Coalescence, combustible fiber aids, deep-bed filtration, oil absorption", Advanced Materials from renewable Resources, U.S. Department of Agriculture, Internal Report, pp. 25, April 1994.
- U.S. Department of Agriculture (USDA), Integrated Taxonomic Information System (ITIS), Texas Agricultural Experiment Station, College Station, U.S.A., 1990
- Wauquier, J.P., 1995. Petroleum refining series", Vol. 1, Editions Technip, Paris, France.