Oil Sorption Mechanism by Natural Sorbents

by

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ABSTRACT

Environmentally friendly absorbents for oil spill cleanup have become popular over the last few years. Natural fibers such as cotton, wheat straws etc. fulfill the need of an environmentally friendly absorbent and a low-cost recyclable material after the cleanup. There are several factors which affect the absorption performance including fiber quality, viscosity of oil, temperature, surface tension, etc. This thesis is focused on comparing absorption performance of 3 types of cotton based materials. Absorption capacity which is defined as the amount of oil absorbed (in gram) per unit amount of sorbent (in gram). Experiments with different combination of oils and cotton based materials reveal were undertaken. Modifications were done to ASTM standard to carry out the experiments in scientific robust fashion and more applicable to oil sorption work.

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CHAPTER I

BACKGROUND

When oil spills occur in the ocean, sea or a river, it creates significant problems towards environmental and ecological balance. The most recent example of an oil spill is the incident in Gulf of Mexico which lasted about 3 months when the BP (British Petroleum) oil rig blew up there on April 20th [1]. The unfortunate incident killed 11 oil rig workers and injured 17 other people and created several other significant environmental issues. A Similar incident happened in Santa Barbara (1969), Gulf of Mexico (1970), Bourne (1979), Arabian Gulf in 1991 [2].

In a typical incident of oil spill, the following problems can happen: (a) It kills a huge marine animal population; (b) It can soil a large area of the beach line; (c) The delay in cleaning the spill can cause further repercussions.

We cannot avoid this problem just by stopping the transportation of oil across the sea; as a large amount of oil needs to be transported every day and there is no alternative for that; This leaves the ecosystem of marine life in a great risk and significant research should be done on minimizing the oil spill possibility and also minimizing the consequences of it.

The cleanup success depends on the simultaneous processes that the spilled-oil goes through after the spill. For example, oil can spread, emulsify, evaporate, disperse, sink or resurface after it has been spilled and the extent of each process affects the hope for satisfactory clean up without much damage. The largest stressor of oil spill is the sea condition at the time of spill or afterwards [3] . For example, a favorable condition of sea towards the spreading and emulsification of oil negatively affects the kinetics of cleaning process.

Several cleanup techniques have been followed in different incident of spill. Selection of the right cleanup technique highly depends on and affected by the high cost process in almost all the techniques. Use of sorbents, burning (in situ), chemical dispersing, and booming and skimming are some popular cleanup techniques that have been used in recent cleanups.

Table 1.1 shows some major incidents of oil spills throughout the last five decades along with environmental and cost effect. The cleanup techniques associated with each incident is also tabulated in Table 1.1.

The use of natural sorbents has its advantages over the other chemical and sorbents and dispersants. The main reason behind its superiority over other sorbents is that its environment friendly and it has better specifications in some important qualities that a sorbent should have; for example, natural sorbent has better oleophilicity, better hydrophobicity. Moreover they are more reusable and more biodegradable. Natural fibers such as cotton, wool, and barley straw are example of natural sorbents.

Here in this thesis, we have observed oil-uptake capacity for three types of cotton as natural sorbent. In addition, the basic properties that the cotton, a biodegradable sorbent, has were too observed such as oleophilicity and hydrophobicity. The experiments that we have done help us understand the oil-uptake capacity of cotton fiber. Moreover, these experiments were done according to the ASTM Standard F726-06 which was explained in details in Chapter five.

This thesis is organized as follows: In the chapter named “Factors affecting Oil Spill control” we have addressed the major influential factors that may affect controlling the oil spill. In the chapter named “Impact of Oil Spill on Health and Environment” we discussed some environmental and health impact of oil spill.

In the chapter named “Methods for Containment and Removal of Spill” we have discussed several techniques for containment and removal of oil spill. Then in chapter named “Experimental Methods and Materials” we have discussed the details of the experiments conducted by us in accordance to a standard test method. In the chapter named “Discussion and Future Research Directions” chapter we’ve reported our data outcome regarding the absorption capacity and performance of different types of cotton absorbents along with discussion about future research directions on this area.

Table 1.1: A Summary of Some Oil Spill Incidents and Their Consequences.

Incidence	Spill Amount	Affected Area	Cost	Effect on Environment	Techniques to Cleanup
Torrey Canyon off the English Channel in 1990 [4]	Crude Oil, 120000 tons	Coast Line (100 miles)	-	25,000 birds died (estimated amount)	-Natural weathering. - Bombs, which ignite fire for in-situ combustion of remaining oil before it spread. - Straws and gorse (used on many of the sandy beaches to soak oil) - Dispersant.
Liberian Registered Tanker (at Chedabucto Bay, Nova Scotia) in 1970	16000 tons	Coast Line (190 miles)	-	-	- Skimmers successfully in sheltered waters. -Sorbents (peat moss); straw was also used. - Dispersants was unsuccessful to penetrate thick layers of oil which formed because of low temperatures and weathering; - In-situ burning was successful on beaches and also on isolated slicks - Floating booms were also unsuccessful.
Amoco Cadiz (off the coast of Brittany, France) in 1978 [4]	light crude, 230000 tons	Coast lines 300 km Beaches polluted	$282,000000 (including a fine amount of $85000000)	3450 sea birds were killed. More affected things are fisheries, seaweed, oysters etc.	- On the shore, oil removed mechanically and manually - Pressure-washing with hot water - Beaches were sprayed with artificial fertilizers and bacterial cultures. - Rubber powder and chalk sinking agents were also used - Microbial degradation
Exxon Valdez (in Prince Williams Sound Alaska) in 1989 [5]	10900000 gallons	coast line (1900 km)	About $7 billion fines were collected, and $2.1 billion of this fine was used for cleanup	250000 sea birds died, Also 2800 sea otters and 250 bald eagles and 22 large (killer) whales.	- Dispersant unsuccessful because much of the oil turned to mousse - Sorbents (as mechanical means were less practical) - Warm water flushing of the beach (consequences unfavorable) - In-situ burning was successful but could not continue because of change in oil state as a result of the storm - Bioremediation enhancement agents were very effective in cleaning (true for over 70 miles of shorelines.) - Booms
Gulf war 1990 [6]	1000000 tons		-	20000 sea birds were killed in this incident	-
Sea Empress in 1996 [7]	Over 70 thousand tons	Coast line (100 km)	$60 million was collected as fine and about $38 million of this fine was used for cleanup	2200 birds were killed. Also, sea weeds and, shell fishes were affected	50% of oil was dispersed naturally. Also some oil were removed mechanically and some were dispersed with the help of chemical dispersants
Gulf of Mexico (BP) in 2010 [5]	208500000 gallons	Shorelines (790 km)	$5.4 billion fines among this fine, $21 billion is for gross negligence [9]. $20 billion for compensation and clean up [1]	997 birds died; also 400 sea turtles died with 47 mammals (including dolphin dead)	- Skimmers and booms - Burning (controlled) - Dispersants.

CHAPTER II

FACTOR AFFECTING OIL SPILL CONTROL

2.1 Sea Condition

The most important factor which affects the spill control is the sea condition immediate after the spill happened or during the time of cleanup. These conditions include wave height and wave periods. It renders most booms ineffective when wave height becomes 1-2 feet and period becomes 1-3S. 6 feet high wave can make the effort of small vessels ineffective for example [10]. For rough and grounding seas, cleanup effort was hampered and delayed for two weeks in the Amoco Cadiz incident due to the sea condition [11].

2.2 Wind Velocity and Direction

Slick movement over open water is controlled by mostly wind velocity and direction. Oil is spread by wind in ocean. The effect of wind is 3-10% more than current and wave of ocean [12]. To reduce the area of confinement, early initiative is necessary otherwise it all would end up in covering hundreds of square miles. It is also necessary to keep the oil from entering drains and sewers or drinkable water courses [13]. Local wind data will be a great advantage for controlling the effects of wind [10].

2.3 Current and Tides

Floating booms cannot withstand one or more knot of sea current velocity [10, 12]. Large tidal ranges also make it more complicated for shoreline cleanup. Hence, to get highest possible outcome in oil spill cleanup, gathering data for sea current and tides is very important.

2.4 Temperature and Atmospheric Condition

Chemical dispersant which acts on highly viscous and ticker crude oil rely on both lighter and heavier fractions of oil; hence evaporation of lighter fractions of oil due to high temperature makes it harder for the chemical dispersant and it becomes unable to sustain combustion [10, 14]. Another important thing is to find the correct affected area. Weather conditions such as rain, fog etc. make it harder to access these areas and hence hamper the cleaning processes.

CHAPTER III

EFFECT OF SPILL-CONTAMINATED WATER ON HEALTH AND ENVIRONMENT

Water contaminated by oil spill is pollutants of environment regardless of their origin (natural or synthetic sources of water). Untreated contamination creates health hazards by creating adverse effect on aquatic organisms. It is also harmful for the economy because it creates adverse effect on tourisms by its unpleasant odor and view along with coating properties. Almost all of the studies that have been done on spill-contaminated water are focused on hydrocarbon oil spill in sea environment. Some findings along these studies are as follows:

3.1 Bioaccumulation

Marine food chain makes it easier for transferring the spilled oils towards human body which has severe adverse effect on human health [15]. These effects involve cancers and Geno-toxic damages in human consumers. Table 3.1 summarizes some studies on effects of spill-contaminated water due to transfer through food chain.

Table 3.1: A Summary of Some Studies on Effects of Spill-Contaminated Water

Accident reference	Study characteristics	Methods	Results
Erika [16]	In vitro Geno toxicity of an Erika fuel extract in human epithelial bronchial cells and human hepatoma cells	DNA adducts Adducts formation and induction of CYP 1A2, COX2 and 5-LOX in hepatoma cells, formation of LT B4 in bronchial cells CYP 1A1, 1A2, 1B1, 2C9, COX1, COX2 AND 5-LOX protein expression LT B4 and PG E2 detection	Adducts formation and induction of CYP 1A2, COX2 and 5-LOX in hepatoma cells, formation of LT B4 in bronchial cells
Erika [17]	Geno toxicity associated with Erika oil-contaminated mussels consumption in rats fed daily for 2 and 4 weeks	Comet assay in hepatic cells, bone marrow and blood cells	Dose–effect–time relationship in hepatic and bone marrow cells. No effect in blood cells
Erika [18]	CYP 1A1 induction associated with Erika oil-contaminated mussels consumption in rats fed for 2 days	CYP 1A1 mRNA expression and EROD catalytic activity in liver	CYP 1A1 mRNA and EROD activity transient Induction

3.2 Direct-contact effects

Hydrocarbon impact on human health due to bare-handed contact with oil is really detrimental. Urinary volatile organic compounds and polycyclic aromatic hydrocarbon levels are found to be increased inside the cleanup workers and volunteers which is responsible for skin tumors if exposed for a long time.

3.3 Adverse effect on oxygen supply

Hydrocarbons create an impenetrable layer in sea surface which hampers the oxygen supply to aquatic organisms [19]. It also creates toxic effect on microorganisms which are responsible for biological treatment of the spill-contaminated water.

CHAPTER IV

METHODS FOR CONTAINMENT AND REMOVAL OF SPILLS

Following are the popular cleanup methods for containment and removal of oil spills:

4.1 In situ Burning of oil slick.
4.2 Mechanical Methods (physical removal).
4.3 Bioremediation.
4.4 Chemical Methods (dispersants).
4.5 Sorbents.

The best choice of methods depends on type of oil, sea surface, soil surface, weather conditions, sea condition, etc. It's also customary to combine multiple methods to beat the underlying conditions [20].

4.1 In situ burning of oil slick

In situ burning is a technique of burning a thick oil layer on a surface of water and effectively reducing the amount of oil on the surface. Here are some important things about in situ burning:

(i) 100-300 tons of oil per hour was the removal rate [21].
(ii) First ignition is done through the help of helicopter using an ignition device suspended underneath it.
(iii) A fireproof boom is placed around the oils to contain oils in surface and to monitor the burning and control it [22].

Following conditions are necessary for a successful In situ burning:

(i) Oil slick should be sufficiently large and wide to burn a large volume of oil
(ii) Then oil itself should be thick enough to sustain combustion.

(iii) Sea water condition should be favorable; i.e. the water should remain calm throughout the process. In situ burning could be hazardous in a stormy weather.

Limitations of In situ burning are as follows. These are also summarized in Table 4.1.

(i) In situ burning is not that effective if it is not done at the earlier phase of the spill because after a long time has passed it becomes harder because of evaporation and natural dispersion.
(ii) Effective wave length for favorable in situ burning is only <3 feet.
(iii) Minimum slick thickness has to be 2-3 mm.
(iv) Evaporation has to be <30%

Some challenges related to In situ burning are as follows:

(i) Loss of lighter fraction can make the burning difficult.
(ii) Complete success is not possible due to sea condition.
(iii) It generates large amount of smoke.
(iv) Viscous residue of burned oil is harmful for the sea bed and marine life. It can also wash away into the shorelines and creates environmental issue.
(v) Secondary fire is always a safety issue [23]. Also, airborne irritants like carbon monoxide, sulfur dioxide are created during burning.

Despite all the limitations and challenges related to in situ burning, this method is very effective, popular and the cheapest technique available. Also it is permissible throughout the world in different governments.

Table 4.1: Comparative Details of Oil Spill Control Methods:

Method	Material	Sorption capacity	Limitations	Area of application	Environment effect	Cost
Sinking materials [24, 25, 26, 27]	Powdered or Granular	Not effective	The retention capacity is not certain. It may also release some fraction while it travels down sea bed. Also, it's non-biodegradable	This is banned in most of the countries	They Contaminate sea beds and fishes	It's expensive
Sorbents (Sorption) [28]	Mineral or Synthetic or Organic	Sorbs up to 80 times Sorbs up to 100 times Sorbs up to 80 times	This is not biodegradable and they degrade very slowly. There is no effective means of recovery and spreading	It's effective on both offshore and shoreline	Environment friendly Not environment friendly It's Eco-friendly	It's expensive It's expensive It's very Cheap
Bio-remediation [29,30]	Biological materials	It's very efficient	This is only limited to biotic environment. It's also ineffective in spill in large and coherent mass.	Its effective on shorelines, wetlands and marshes	Environment friendly	It's cheap
Dispersants [31, 32, 33, 34, 35]	Chemical materials	This method is efficient with Spray from helicopter. It can treat large sea areas	This is very little effective on highly viscous oil. It's also ineffective in calm water.	It's g ood in calm, harsh and very deep water body. It allows sufficient amount of dilution	Aquatic flora and fauna gets harmed by this method	It's expensive
In situ burning [28, 35, 36]	Bombs or explosives, Also fire resistance booms and sometimes liquid fuel	It's efficient in removing large quantities of in a less amount of time and it's effective before weathering	Effective if the wave's height is less than 3 ft. Minimum slick thickness is 2 to3 mm. Less than 30 percent evaporation losses. Emulsion of less than 25% water content. Also not able to sustain/maintain complete combustion of slick. Viscous and dense residue of combustion damage sea bed and shorelines and beaches. It's also a source of secondary fire.	It can be used on water body and on land.	It's very harmful near residential areas and also near flammable structures. It emits toxic compounds such as carbon monoxide, sulfur dioxide, and PAHs during combustion of oil on water. It also causes air borne diseases.	This one is the cheapest
Booms & skimmers [37, 38, 39]	Mechanical equipment's	It's efficient	Structural failure can happen. Also time consuming and expensive. Moreover oil slick escape at slick velocity up to 1 knot can happen.	It can be used only on water and it's effective only in calm sea.	Environment friendly	It's expensive

4.2 Mechanical methods

By using booms and skimmers in removing oil from sea surface, it can be of advantage over chemical dispersants in terms of adverse environmental effects. The following points are pertinent to mechanical methods.

(i) V shaped barriers are created by combining V shaped barriers and this effectively concentrate the oil which is picked up by skimmer bags and boats [12, 40].

(ii) This method is more effective in low temperature because oil gets thicker and more viscous in low temperature which increases skimmer efficiency.

(iii) Oil recovery is improved by high rotation of skimmers.

(iv) Sorption capacity of the material used in skimmer is significant on efficiency of recovery.

The following are some common limitations of the mechanical methods:

(i) This is an expensive method

(ii) Needs large workforce and expensive equipment.

(iii) Boom drainage failure happens if boom draft lies lower than the oil slick. Some other common failures are failure of droplet entrainment and failure of critical accumulation [41, 42].

(iv) Only effective in calm water condition with very little wind velocity

Details of the mechanical methods and its limitations are compared too in Table 4.1.

4.3 Bioremediation

In Bioremediation process, small bio organisms break complex bonds of spilled oil for food purpose. So artificially inserting bio organisms into spilled oil and let it break the oil composition naturally is a great way of oil spill cleanup without adverse environmental effect. To expedite the process, it is possible to introduce fertilizers and nutrients to the bio organisms and also introducing non-native microorganisms. That's why these microbes are often called oil eaters. It is a very effective for the cleanup. Some details are compared with other methods in Table 4.1.

Some limitations of this technique include the following:

(i) Ineffective in removing large coherent masses of oil [43].
(ii) It is affected abiotic environmental factors such as fixed forms of Nitrogen, insufficient oxygen and low temperature of water [29].

4.4 Chemical methods (dispersants)

The main advantage of chemical dispersants over other methods is that it can be applied to larger areas. The intermolecular attraction and tension between the oil and the water is reduced by surfactants which are present in the chemical dispersants. Here are some important facts about the use of dispersants:

(i) It's generally applied by spray equipment by help of helicopter.
(ii) Effective time of oil disappearance is dependent on successful application of Dispersant and specific spray process [10].
(iii) Dispersant has low effectiveness in calm water because it does not get enough energy to break the tension between the water and the oil.
(iv) United States does not promote using Dispersants due to its doubtful effectiveness issue and toxicity issue on environment.

(v) It has adverse effect on human health if it's carried to human through fish. These effects include respiratory, nervous, renal problems in human.

Comparison of costs, effectiveness etc. of this method with other methods is in Table 4.1.

Some limitations of applying chemical dispersants include:

(i) Use of dispersants is expensive.
(ii) Dispersants contain toxic compounds harmful to both human and marine life.
(iii) These are ineffective in calm water.
(iv) Not greatly effective in a thinner oil slick [33].

4.5 Sorbents

Materials which are oleophilic and hydrophobic are called Sorbents because of its high capacity of sorbing oil and rejecting water. Sorbents generally can be categorized as follows [12, 44, 45].

(i) *Synthetic organic sorbents*: It is the most widely used sorbents; it's found from high molecular weight polymers. It has good hydrophobic and oleophilic properties. Example of this kind of Sorbents include: polyurethane which are ultralight and open cell foams and these are capable of sorbing oil in 100 times of their own weight. Another example is tire powder which is capable of sorbing 220 grams per gram of sorbent and even after recycling 100 times.

The prime limitation of this type of Sorbents is non-biodegradability. Several techniques can be applied to overcome this limitations but this include incorporation of several machines which are added cost to the system.

(ii) *Inorganic mineral sorbents*: Also known as Sinking Sorbents. Normally greatly dense and also fine graded minerals. Main purpose is to sorb floating oils. Examples can be stearate treated chalk, fly ash (silicon treated), graphite's, zeolites silica gel, silica etc.

Activated carbons belong to three types of origin: botanical origin, mineral origin or polymeric origin. These activated carbons are cheap and frequently available. They have a very large surface area, higher surface reactivity and perfect pore sizes. Another type can be organoclays which sorbs diesel, hydraulic and engine oil and has high hydrophobic and sorption property. These are expensive but very effective than activated carbons. So, a good idea is to use a mixture of activated carbons and granular organoclays, so that effectiveness of activated carbons can be increased with organoclays.

The bad side of mineral sorbents includes contamination of sea beds and harmful effect on marine habitats. Release of sorbed oils while sinking is another limitation of this kind of sorbents. Fire risks, pore clogging etc. can be added to this list for activated carbons. All limitations and details are compared in Table 4.1.

(iii) Agricultural products: These are also known as natural organic sorbents. These are mainly natural oil or wax; and hence when it is dry, it is very light weight and float in water. When applied with oily water, it joins with oil and sinks with the oil. These types of sorbents are cheap, environment friendly, easy to find and eco-friendly. Some examples can be cotton, kenaf, sugarcane bagasse, cotton grass fiber, saw dust, banana pith etc. These are more efficient than some of synthetic organic materials.

One specific example of agricultural product s is a Straw which is a hollow and floats longer on water. It floats long enough to collect sufficient amount of water which is the reason for becoming the most widely used sorbents.

Although some synthetic materials are more effective than agricultural products, high availability, low cost and bio-degradability makes these natural organic sorbents very popular.

Despite the advantages, natural organic sorbents have some limitations; cost involved in recovering the oil soaked sorbents is very high. Moreover, for some agricultural products, it is necessary to spread dry sorbents and retrieve the oil soaked ones manually. These makes it time consuming and hence expensive and incapable of being used in large amount of spill.

CHAPTER V

EXPERIMENTAL METHODS AND MATERIALS

5.1 Characterization of cotton linters

Cotton fiber has physical and chemical properties which makes it a perfect absorbent.

One of the important physical properties of cotton is that it has a great tensile strength i.e. cotton is moderately strong fiber [46]**.** It's inelastic and has low specific gravity. High moisture regain and absorbent capacity makes it remarkable sorbent. Other physical properties include resistance to degradation by heat and sunlight and less of strength over its age.

Along with the physical properties, cotton has some excellent chemical properties. For example cotton does not get affected by acids. Moreover it has excellent resistance against alkalis. It also has high resistance to organic solvents. Cotton has resistance against insects which protects it from attack of moth or other micro-organisms. Due to all these physical and chemical properties together, cotton is the most popular sorbent for oil cleanup.

All the physical and chemical properties of the cotton outlined above are very important in identifying the type of the fiber. Nevertheless, researchers have characterized the cotton fibers for research purposes in terms of its micronaire values, which are the fineness and maturity [47]. The fineness represents the linear density of the fibers (measured in millitex). The maturity stands for the degree of cellulose deposition. Research studies reported that there is reversal proportionality between the micronaire values and the sorption capacity. For instance, the lower the micronaire of the fiber; the lower its maturity; the higher its surface wax content, the finer the fiber, and hence the higher its sorption capacity [48, 49]

The cotton fibers that were studied were as follows:

(i) Absorbent 1
(ii) Absorbent 2
(iii) Absorbent 3

Absorbent 1 is used for commercial purposes. It is a processed fiber where its basic properties have been modified. As for Absorbent 2 and Absorbent 3, they were obtained from Pyco industry's branch in Lubbock, Texas. These sorbents still preserve their natural properties such as oleophilicity and hydrophobicity.

5.2 Characterization of oil used

Any oil can be characterized based on different physical properties such as viscosity, density, surface tension.

Viscosity: Viscosity is a unique physical characteristic of a liquid or gas which measures the resistance to flow [50]**.** A falling object through maple syrup will face more resistance than through vegetable oil. We can measure viscosity by determining the rate of flow of that fluid material through a small diameter tube or path. The volume (V) of a fluid material transported per unit time (t) is proportional to the pressure (P) which is pushing the fluid, the length (l) of the carrying path, the width of the path (radius, r) and lastly its inversely proportional to the viscosity (η) of the fluid.

Typically, viscosity (η) can be denoted mathematically as follows:

$$\eta = \frac{\pi r^4 P t}{8Vl}$$

The unit of viscosity is Poise.

Density: It is the amount of oil mass (m) per unit volume (V). The denser a material is, the heavier it becomes in unit volume. The density, 'd' can be written as:

$$d = \frac{m}{V}$$

The unit of density in SI is g/cm^3

Surface tension: Surface tension is a net force working on the surface of a liquid which controls the shape of that liquid. It creates because of uneven force acting on surface molecule of a liquid from bottom molecules of that liquid and upper molecule of the gaseous material which is in contact with the liquid surface. This is a very important physical property of a liquid which affects the sorption quality of a sorbent. The unit of surface tension is (mN/m).

Based on viscosity, density and surface tension, Oil types that were used as substrates to evaluate the sorption capacity performance of the Absorbent 1, Absorbent 2, and Absorbent 3 can be characterized at room temperature into the following categories in Table 5.1.

Table 5.1: Characteristics of Studied Oils at Room Temperature

Oil	Viscosity (cP)	Density (g/cm^3)	Surface Tension (mN/m)
Texas Raw Crude oil 2012	30	0.972	30.39
Non detergent motor	139.8	0.925	31.44
Canola oil	50.2	0.917	32.91
Peanut oil	64.13	0.910	32.91
Engine oil	175	0.885	31

5.3 Oil sorption testing method

The following are the method followed for testing the oil sorption capacity according to American Society for Testing and Materials ASTM 726-06 [51]. It is a standard method that can be applied for laboratory tests to comprehend the practical performance of sorbents in uptaking the oil or other floating liquids from the surface of the water. This standard test method is illustrated in the following steps:

(i) 0.5-0.6 g of cotton samples were placed in a stainless steel mesh in a circular shape.

(ii) Oils are taken in a dish. The approximate amount of oil was 1500 mL.

(iii) The entire mesh with the sample cotton is then immersed in the oil dish in such a way that circular mesh move freely into the oil.

(iv) Then the dish is covered with glass plate.

(v) With the help of a centrifuge table, the entire set up was centrifuged at 75 rpm for 20 minutes which eventually creates a dynamic environment.

(vi) After centrifuging, the oil soaked cotton was removed and drained for 15 minutes.

(vii) The excess oil adhered to the surface of the sorbent was removed

(viii) The sample was then weighed in a weighing table.

(ix) The total procedure was repeated 10 times and average of all the values are taken to nullify measurement errors.

The oil sorption capacity is then calculated using the following equations:

$$oil\ soprtion\ capacity = \frac{W_f - W_0}{W_0}$$

Here, W_0 is the initial weight of the dry sorbent and W_f is the weight after the sorbent is soaked with oil.

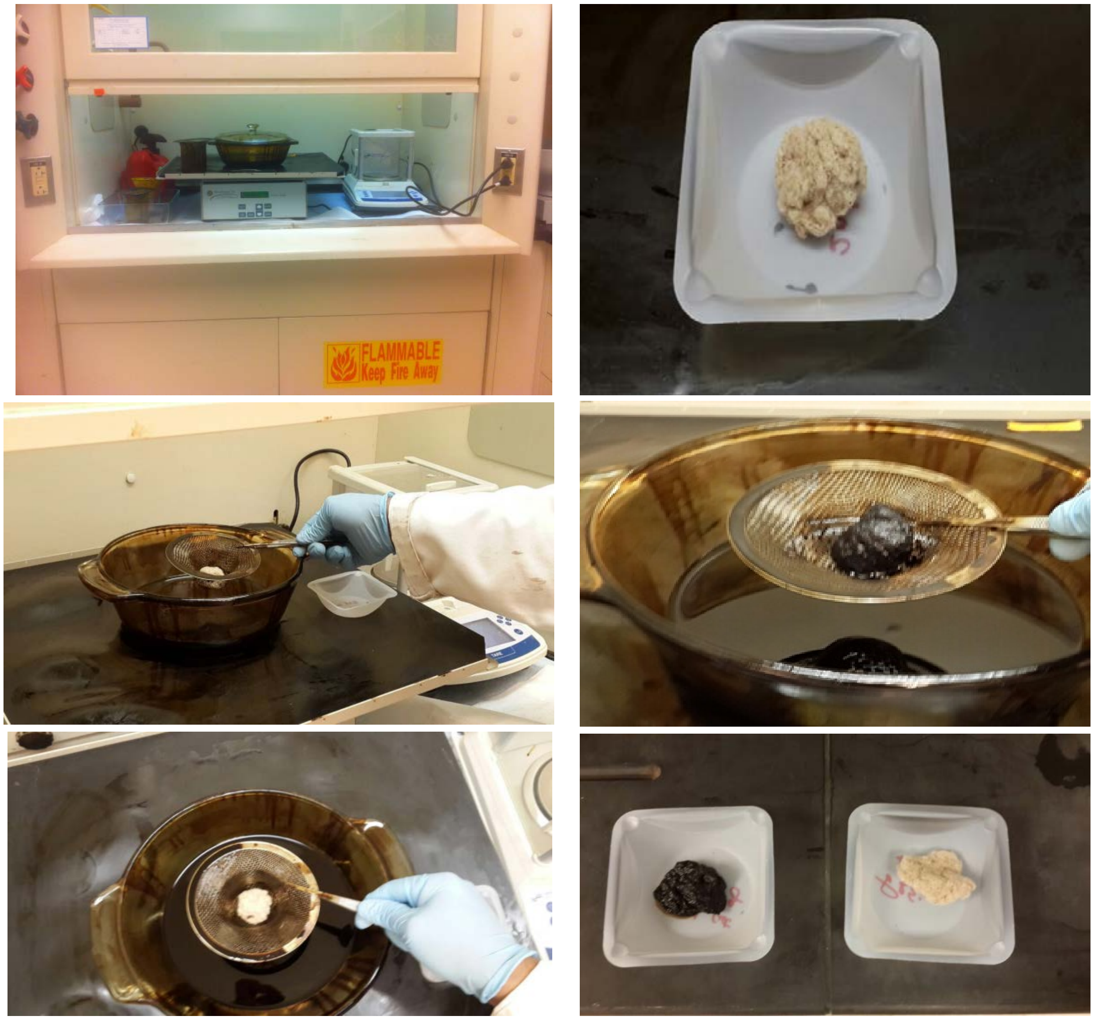

Figure 5.1: ASTM Standard F 726-06 Test Method for Oil Uptake Operation

5.4 Water sorption testing

The practical performance of the sorbent was further tested with water sorption testing. But unlike oil sorption testing, we have used static method of the testing which means there was no involvement of centrifuge machine or rotating system. So the same procedure like oil sorption testing in section 5.3 was applied for water sorption testing except the use of centrifuge. And of course, instead of oil, we have used water as the material where we soak the sorbent into. The ultimate reason for applying the static case is basically to observing the natural sorbents characteristics in general which floating, soaking, being repellant to the water due to its oleophilic and hydrophobic properties.

CHAPTER VI

DISCUSSION AND FUTURE RESEARCH DIRECTIONS

At the very beginning of this chapter, we'll present our result in figures and tabulated form.

First data outcome, Crude Oil average sorption capacity by the cotton sorbents used for testing is showed below in Table 6.1.

Table 6.1: Average Sorption Capacity of Crude Oil by Absorbents

Sorbent	Average Sorption Capacity of Crude Oil (g/g)
Absorbent 1	19.95
Absorbent 2	18.81
Absorbent 3	13.49

The result is also schematically shown in the following figure. It can be clearly seen that "Absorbent 1" has the highest sorption capacity for Crude Oil. This is because of the fact that Absorbent 1 is used commonly for commercial purposes unlike Absorbent 2 and 3 which were obtained from Pyco industry, Lubbock, TX. Most importantly, Absorbent 1 is processed cotton which means that the physical and chemical properties have been modified resulting in a high sorption capacity among the rest of the Absorbents used for testing.

According to Figure 6.1, Absorbent 1 has lower micronaire values than that of Absorbent 2 and Absorbent 3 which in turn result in higher sorption capacity. This observation corroborate well with the finding that there is a nonlinear relationship between the micronaire values and the sorption capacity [47]. Additionally, a statistical analysis was performed using three samples t-test to conclusively show the significance and the standard deviation in the crude oil sorption capacity of all Adsorbents.

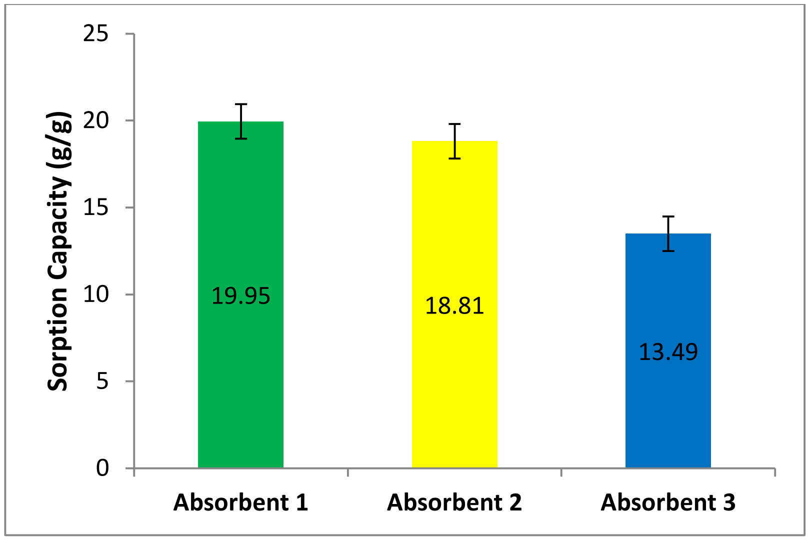

Figure 6.1: Average Crude Oil Sorption Capacity for All Absorbents

Secondly, water sorption capacity by the cotton Adsorbents are found in two different systems: Dynamic and Static to be as the following in Table 6.2:

Table 6.2: Water Sorption Capacity by Absorbents in Dynamic and Static System

System	Sorbent type	Water Sorption Capacity (g/g)
Dynamic	Absorbent 1	20.94
	Absorbent 2	11.90
	Absorbent 3	11.53
Static	Absorbent 1	20.75
	Absorbent 2	4.72
	Absorbent 3	4.53

To further evaluate the practical performance of the Absorbents, an additional test was performed for calculating the Absorbents water uptake capacity. This procedure involves two environments which are Dynamic and Static system. The main reason for introducing these systems is basically coming from the fact that the oil spill mostly occur in open water. By applying the Absorbents into static water system, we can assess the Absorbents qualities that include both hydrophobicity and oleophilicity. Furthermore, the dynamical system benefits for knowing how well the Absorbents have a greater affinity for oil than water. It is evident that the tested Absorbents when they are dry, they have less weight; and when they applied to an oil-water system, they tend to float carrying the oil with them. Additionally, it is observed in Figure 6.2 that the Absorbents 1 since it is processed cotton was immediately sunk in water for both the static and dynamic system causing a higher sorption capacity. On the other hand, Absorbents 2 and 3 for the dynamic system show statistically significant water sorption capacity higher than that of the static system.

To comprehend this phenomenon, the dynamic environment causes the Absorbents' characteristics to partially or fully break into the water molecules. The major characteristics include hydrophobicity, oleophilicity, and pore volume of the Absorbent, fiber lumen, size, bulk density, and surface area. All these factors effect on the sorption capacity performance either collectively or individually.

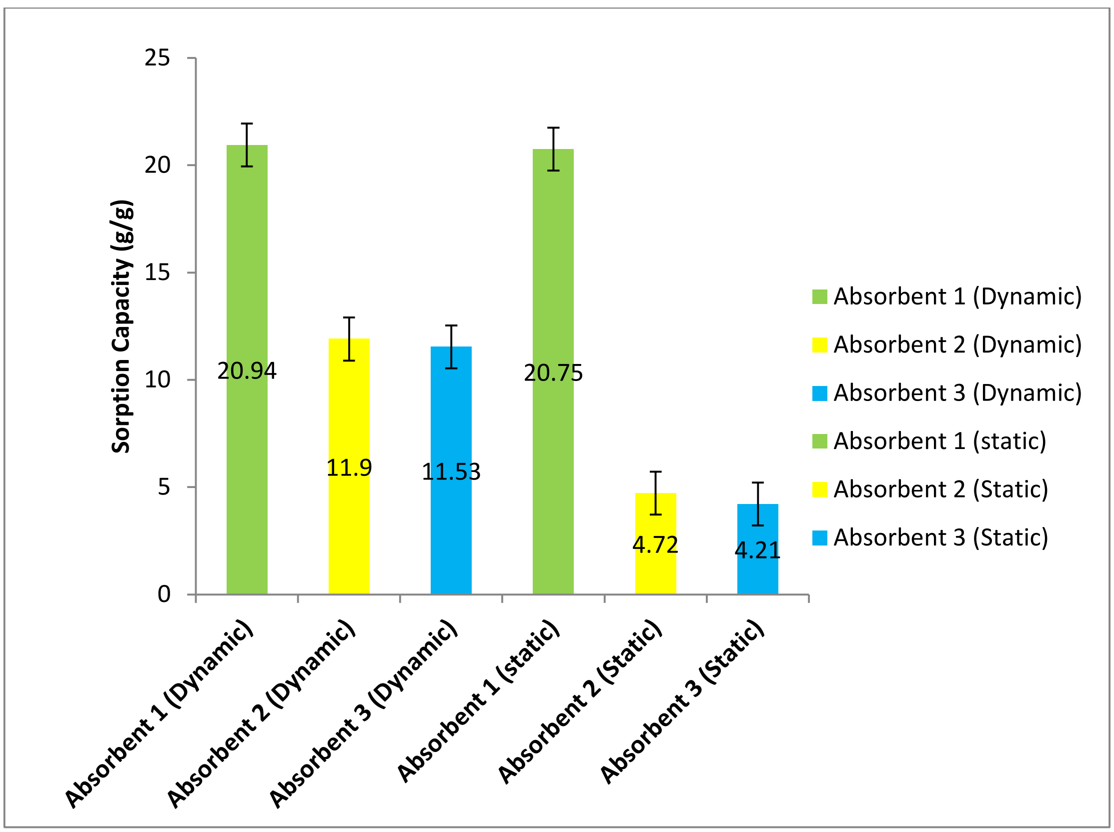

Figure 6.2: The Effect of Dynamic and Static System on the Water Sorption Capacity for All Absorbents

Thirdly, the absorption capacities for Pyco industry samples, Absorbent 2 and Absorbent 3, over all type of sorbets used in this study are shown in the following Table 6.3.

Table 6.3: Multiple Sorbates' Sorption Capacity by Adsorbents Two and Three

Sorbent	Sorption Capacity by multiple sorbate (g/g)					
	Peanut Oil	Motor Oil	Canola Oil	Crude Oil	Engine Oil	Water
Absorbent 2	20.93	18.61	18.77	18.81	18.87	11.9
Absorbent 3	14.39	15.48	14.61	13.49	11.91	11.53

The schematic sketch of the sorption capacity for these Adsorbents is as follows in Figure 6.3:

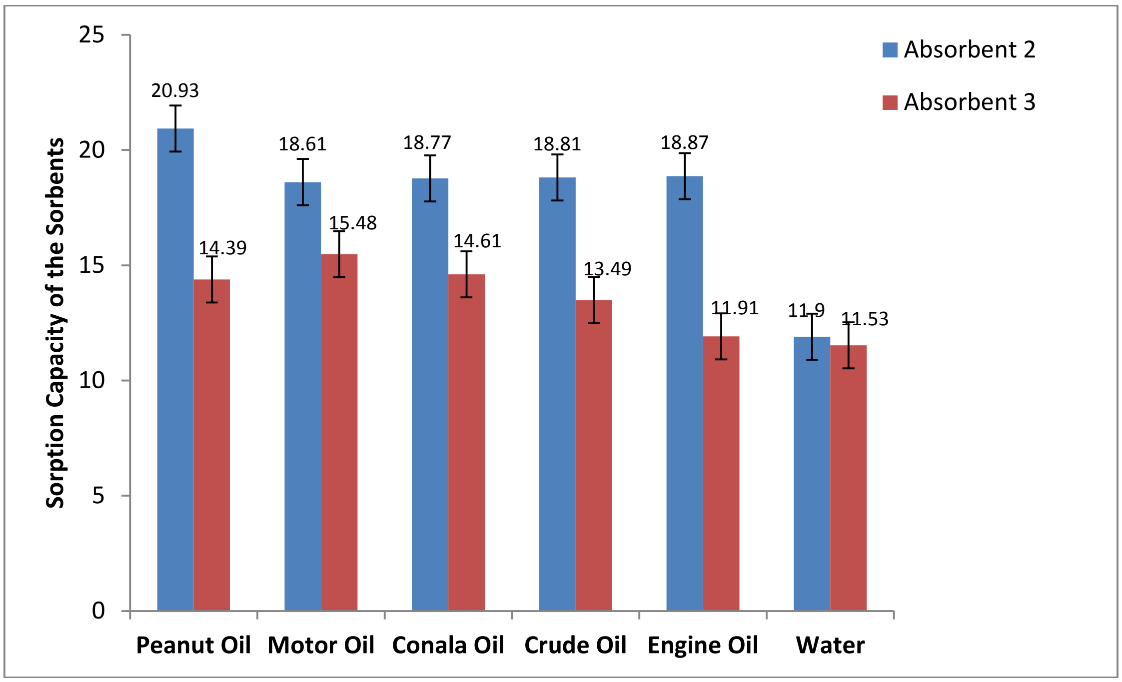

Figure 6.3: Sorbets' Sorption Capacity for Absorbents Two and Three

Figure 6.3 depicts that both Peanut Oil and Motor Oil's sorption capacity are being highest among the rest of the sorbets. This is basically a consequence of the physical properties of the Oils tested explained in the previous chapter Table 5.1 Motor Oil has relatively high Viscosity which means that the Motor Oil resists being flown causing the Absorbent 2 and Absorbent 3 to uptake the motor oil within their fiber matrix. However, since the Motor Oil has nearly low surface tension "interaction", both Absorbents 2 and 3 have more capability to sorb Oil. Moreover, Peanut Oil has low viscosity but it has the highest Surface Tension in association with Canola Oil.

In the Figure 6.3, it was also evident that water has the lowest sorption capacity for both Absorbent 2 and Absorbent 3. Perhaps the feasible explanation for this is that both Absorbents are sorbable to the Oil and repellant to the water.

Finally, the combined sorption capacity of all sorbets by all Absorbents used is showed:

Table 6.4: The Effect of All Sorbets Used on the Sorption Capacity for All Absorbents

Sorbent/Sorbate	Sorption Capacity by multiple sorbets (g/g)					
	Motor Oil	Peanut Oil	Crude Oil	Canola Oil	Engine Oil	Water
Absorbent 1	23.01	21.58	19.95	19.62	18.28	20.94
Absorbent 2	18.61	20.93	18.81	18.77	18.87	11.9
Absorbent 3	15.48	14.39	13.49	14.61	11.91	11.53

Schematically, we have showed like this:

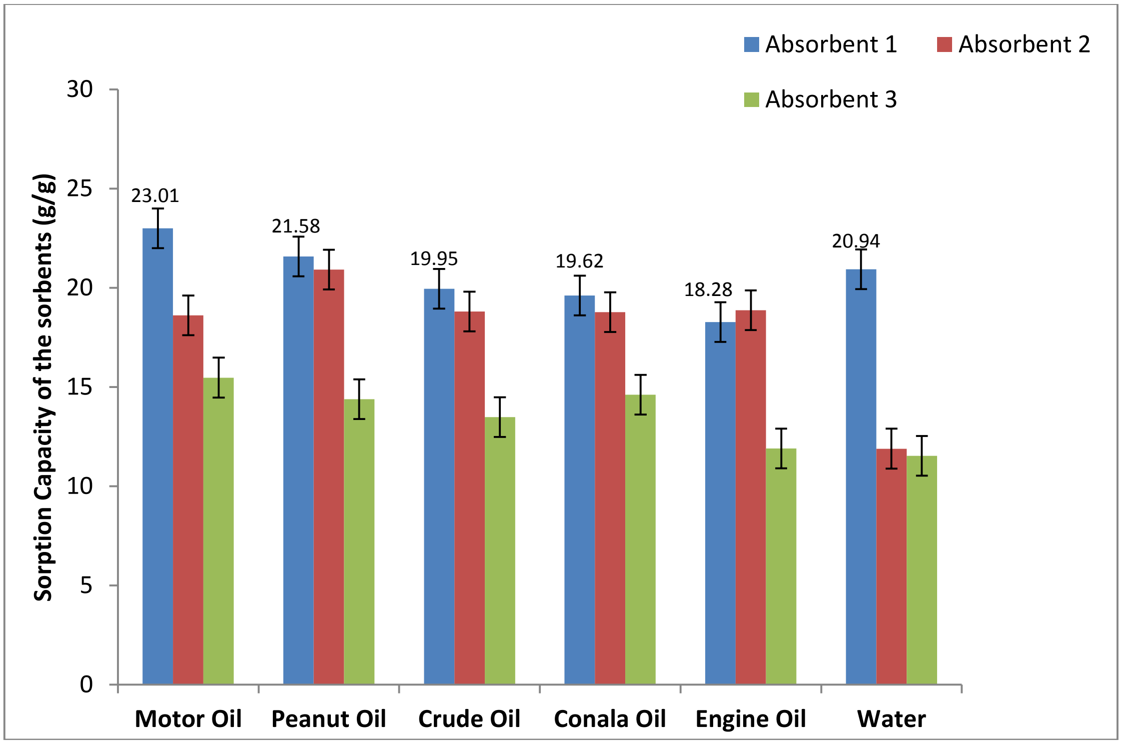

Figure 6.4: The Combined Sorption Capacity of All Substrates by All Absorbents

Figure 6.4 shows the sorption capacity of all Sorbets by all Absorbents tested.

Again, both Motor and Peanut Oil have the highest sorption capacity whereas the water has the lowest as it always does. The correspondence between the Oil physical quantities' values and the Absorbents fiber characteristics result in either higher sorption capacity like Motor Oil or lower sorption capacity like the case in Engine Oil. Further, the lower the micronaire in the cotton fiber, the less cellulose deposition due to its immaturity; and hence the higher its sorption capacity. Most importantly, both an increased fineness and a higher surface wax content lead to more sites for all sorption mechanism to be taken place. These mechanisms are usually named the absorption process.

In the process of absorption, the sorbate molecules accumulate into the surface of sorbent; it does not penetrate the sorbent materials. So absorption process is of three fold: (i) Oil diffusion into the sorbent molecule (ii) sorbate molecule getting trapped into the sorbent structure (iii) droplets of sorbate getting agglomerated into the rough and porous structure of the sorbent [52].

The word "absorption" can be physically understood by the attraction between the sorbate and the outer surface of the sorbent. Due to the obvious reason and from definition of "absorption", it is easy to understand that surface tension of sorbent, sorbent quality; viscosity of the sorbate affects the absorption process the most [52].

The rate of spreading of oil into sorbent's structure is directly related to the surface tension of the oil. Decreasing the surface tension increases the absorption rate. Chemical bonds or some specific functional groups have great impact on absorption rates. Example of these groups are C=O, C-O, O-H [52].

A low viscosity of oil favors the absorption quality because high viscous oil tends to slow the leaching of sorbed oil into sorbent surface; Moreover, viscosity is by definition known as resistance to flow [50].

A change in temperature can change the absorption performance of the sorbent. Generally, an increase in temperature favors the absorption process. But opposite can also happen.

In our experiments we have chosen "cotton" because of the advantages it has over other sorbents. These advantages are discussed in Chapter five. The most significant effect on absorption process by cotton is the micronaire values of the cotton fiber and our experiments are designed to mainly compare absorption capacity of different types of cotton with the sorbate being same. We have also done experiments with different types of sorbets and absorbents. So effectively we have observed how the oil sorption is affected by fiber quality change, oil viscosity change and surface tension change.

We have shown our results in terms of oil sorption capacity of cotton (g/g) which is the best way to compare absorption performance. We have used three types of cotton and 6 types of sorbets. Performances are shown above in this section and from the results we can see that, “Absorbent 1” which is the best quality cotton gave the best performance under similar circumstance compared with “Absorbent 2” and “Absorbent 3”.

Until recently, a large number of research studies have been conducted and lot is going on to find the effectiveness of natural products as perfect oil absorbents. To improve the oil absorption performance using natural products like cotton, straw etc. Research must go on for improving the limitations they have against absorption. Research can also go on to find perfect combination of fiber type and oil/sorbate. Also, research can be done to ensure if a fiber in a certain environmental condition is suitable for absorbing specific types of oil.

To reduce cost in use of cotton or other natural products, recyclability is a big issue. So it’s still an open issue to improve recyclability and hence improving absorption efficiency.

The open challenges for spill control also include study in hydrophobicity of sorbents and oils, retention capacity of sorbents, time of storage of oil into sorbents, environmental safety issues, and the application of the natural sorbent and its recoverability [2].

To summarize, we can say that cotton is widely used for being environment friendly, low density and very good hydrophobicity etc. Low micronaire cotton (in terms of absorption quality, it is best type of cotton fiber) generally gives better performance and we have observed the same through our experiments. We have also seen effect of other stressors of absorption practically. More comparisons with other type of sorbents would make this thesis more attractive, but the experiments done here are vital to prove effectiveness of natural fibers and the effect of quality of natural fibers into oil spill cleanup.

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