



INTRODUCTION

1. INTRODUCTION

Marine oil spills are the most important threat to the coastal environment and ecosystems of the sea. Furthermore, oil spills are responsible for the great loss of energy resources. Million of tons of oil are spilled every year, accidentally and deliberately, into the environment during transport, storage and processing of the oil. Several hundred million gallons of oil were spilled into the sea due to the demolition of oil storage tanks in Kuwait in 1991. During the production and transport of oil, accidental or intentional spills occur in water or on land, creating numerous environmental problems for many years. With another recent large spill of oil (about 12,000 tones) on the Spanish coast of Galicia by the *Prestige* oil-tanker, nowadays, there is a growing worldwide concern about the urgent need to control accidental and deliberate releases of oil during transport and storage. Examples of other spilling of oil in recent years include the purposeful dumping of 2.5–4 million barrels into the Gulf of Suez during the Persian Gulf war, the release of 260,000 barrels into the gulf of Alaska by *Exxon Valdez*, the loss of 24,000 barrels into the Monongahela River due to a ruptured storage tank and the Japan Sea and the Straight of Malacca oil tanker accident. The adverse impacts to ecosystems and the long-term effects of environmental pollution by these and other releases call for an urgent need to develop a wide range of materials for cleaning up oil from oil impacted areas especially as the effectiveness of oil treatment varies with time, the type of oil spill, the location and weather conditions [Fingas, 1995]. These spills have major adverse effects on the adjacent ecosystem and also pose detrimental social and economic consequences [Pezeshki et al., 2000, Kim, 2002 and Kingston, 2002]. The methods developed for oil spill cleanup can be categorized into three main

groups. The first group includes physical methods such as adsorbents, booms and skimmers, the second one comprises chemical methods such as dispersion, in-situ burning, and the use of solidifiers, and the third one considers biological methods or bioremediation. Even though no single system is likely to be completely effective, the use of an oil sorbent is one of the most widely used methods for combating oil spills in the sea [Walkup et al., 1969]. Usually, a combination of all these methods should be used to achieve an effective cleanup. Oil spill clean-up sorbents have been historically used to contain oil spilled in the sea. Oil can be sorbed from the surface of the sea by using some suitable sorbent materials. Sorbents have a significant capacity for oil recovery from the surface of the sea, minimum harmful effects on ecosystems, and a low price. Sorbents recover the spilled oil by either adsorption or absorption mechanisms. Adsorption is the distribution of the adsorbate over the surface of the adsorbent. When added to an oil spill, sorbents can change the oil from liquid to a semisolid phase. Then, the oil will be easily recovered by the removal of the sorbent structure. Hydrophobicity and oleophilicity are the most important properties of a sorbent to be considered in oil spill clean-up. Other important factors are the retention over time, the recovery of oil from sorbents, the amount of oil sorbed per unit weight of sorbent, the reusability and the biodegradability of sorbents. These sorbents can be classified into three groups, namely inorganic mineral products, organic synthetic products and organic vegetable products. The inorganic mineral products include perlite, vermiculites, sorbent clay, dolomite, graphite, etc. These materials do not show adequate buoyancy and their oil sorption capacity is generally low. The organic vegetable products are generally natural fibers, such as kenaf, cotton, and milkweed floss. These

sorbents are preferred as they are mostly biodegradable and safe for disposal. Some synthetic products, e.g polypropylene, polyurethane foam, polyethylene terephthalate (PET) and teflon, are also widely used in oil spill clean-up due to their low cost and availability. The oil sorption capacities of these sorbents are generally high and vary depending upon the type of sorbent over a range of 0.26–86 g of oil per unit mass (g) of sorbent. Although a significant portion of oil can be recovered from some sorbents, such as fir fibers and exfoliated graphite, such that they can be reused for a few cycles, the eventual disposal of these sorbents with sorbed residual oil remains an important issue. Incineration or landfilling of sorbents is not desirable due to the adverse environmental effects often associated with these techniques, i.e toxic air emissions and subsurface soil and ground water contamination by oil components [Choi and Cloud, 1992, Setti et al., 1999, Inagaki et al., 2000, Toyoda et al., 2000, Teas et al., 2001 and Inagaki et al., 2002]. For used oil spill clean-up sorbents and contaminated soil, bioremediation may be an effective remediation technique. Extensive studies have been carried out for determining the bioremediation potential of terrestrial soil contaminated with oil [Song and Bartha, 1990, Song et al., 1990, Hutchins et al., 1992, Hess et al., 1996, Harrison et al., 2000, Nocentini et al., 2000, Shin et al., 2000, , Namkoong et al., 2002 and Boopathy, 2003]. However, no significant research, except by [Setti et al., 1999] has been reported for biodegradation of oil sorbed on spill clean-up sorbents. Bioavailability plays an important role in biodegradation of oil. In two-phase systems (water–oil), several studies have indicated that the rate of dissolution from a NAPL (non-aqueous phase liquid) determines the rate of microbial uptake and dissolution is facilitated by microorganisms

producing external biosurfactants and bioemulsifiers [Volkering et al., 1992, Volkering et al., 1993 and Mukherji and Weber, 1998]. Yet other studies have reported direct uptake of oil from the oil–water interface by microorganisms that attach to the interface [Nakahara et al., 1977 and Rosenberg, 1981]. Increased cell-surface hydrophobicity induced in response to growth on a NAPL has been implicated in facilitating uptake. However, in three phase systems when oil is sorbed on a sorbent, its accessibility to microorganisms may decrease further. Several researchers have demonstrated that sorbed compounds initially remain loosely bound on to the soil surfaces or remain in the soil macropores from where desorption is rapid, thus leading to high initial uptake. However, with time the compounds penetrate further and enter into the micropores, and become highly desorption-resistant [Robinson et al., 1990, Harms and Zehnder, 1995, Hatzinger and Alexander, 1995 and Bosma et al., 1997]. A few studies suggest that sorbed compounds are directly available to microorganisms without prior desorption [Gordon and Millero, 1985, Guerin and Boyd, 1992 and Crocker et al., 1995]. This has been attributed to the capability of certain microorganisms to attach to interfaces of sorbed/separate phase substrate using surface structures such as fimbriae and capsules. [Setti et al., 1999] have reported enhanced bioavailability of oil sorbed on oil spill clean-up sorbents such that overall biodegradation was higher in systems with sorbents in comparison to systems without sorbent. This was attributed to improved interaction between the oil and the microorganisms derived from the formation of water–cell–sorbent interfaces.

This section reviews the synthesis and the absorbing properties of the wide variety of porous sorbent materials that have been studied for

application in the removal of organics, particularly in the area of oil spill clean-up. The discussion is especially focused on synthetic and natural sorbents many of which have been demonstrated to exhibit (or show potential to exhibit) excellent oil absorption properties. The areas for further development of some of these materials are identified.

A wide range of materials for oil remediation have actually been employed such as dispersants, absorbents, solidifiers, booms and skimmers. Dispersants simply disperse the oil to accelerate the oil and separate it from the water by absorption. Absorbents collect the oil and separate it from the water by absorption. Solidifiers are dry granular, hydrophobic polymers that react with the oil to form a cohesive, solidified mass that floats on water. Booms and skimmers physically corral the oil for collection. Booms are specifically used to confine the oil to a specific area (containment) or stop the oil from entering a given area (diversion) while skimmers are used to recover the oil from the water surface [Fingas, 1995].

Absorbent materials are attractive for some applications because of the possibility of collection and complete removal of the oil from the oil spill site. The addition of absorbents to oil spill areas facilitates a change from liquid to semi-solid phase and once this change is achieved, the removal of the oil by removal of the absorbent structure then becomes much easier. Furthermore, these materials can, in some cases, be recycled. Some properties of good absorbent materials include hydrophobicity and oleophilicity, high uptake capacity, high rate of uptake, retention over time, oil recovery from absorbents, and the reusability and biodegradability of the absorbents [Reynolds et al., 2001 and Teas et al., 2001]. Several absorbents that exhibit at least some of these properties have been developed e.g. modified

organophilic clays, lime, silica, exfoliated graphite, hydrocarbon and plastic polymers, cellulose-based materials and elastomers [Choi and Cloud, 1992, Lee et al., 1995, Yokogawa and Yokoyama, 1995, Gitipour et al., 1997, Daughney, 2000, Meininghaus and Prins, 2000, Coronado et al., 2001, Reynolds et al., 2001 and Sun et al., 2002]. These materials all show porosity and ability to absorb oil in the presence of water. It has been suggested that oil-sorbent materials can be grouped into three major classes namely inorganic mineral products, synthetic organic products and organic vegetable products [Scharzberg, 1971 and Melvold et al., 1988]. Mineral products include materials such as zeolites, silica, perlite, graphite, vermiculites, sorbent clay and diatomite. Synthetic organic products include polymeric materials such as polypropylene and polyurethane foams which are the most commonly used commercial sorbents in oil spill cleanup due to their oleophilic and hydrophobic characteristics [Schatzberg and Jackson , 1972]. A major disadvantage of these materials is that they degrade very slowly in comparison with mineral or vegetable products and are not naturally occurring as mineral products. Examples of organic vegetable products (or natural sorbents) that have been reported include straw, corn corb, wood fiber, cotton fiber, cellulosic kapok fiber, kenaf, milkweed floss and peat moss. However, Such organic vegetable products have been reported to show poor buoyancy characteristics, relatively low oil sorption capacity and low hydrophobicity. The purpose of this section is to provide a general overview of these three classes of sorbent materials that have been developed for oil spills clean-up with particular emphasis and more detailed discussion on hydrophobic silica aerogels, zeolites, organophilic clays and natural sorbents.

1.1 NATURAL OIL SORBERS

A wide variety of natural sorbents such as rice straw, corn corb, peat moss wood, cotton, milkweed floss, kapok, kenaf and wool fibers have been employed as sorbents in oil spill clean-up [Choi and Cloud, 1992, Moreau, 1993, Choi, 1996, D'Hennezel and Coupal, 1972]. These natural sorbents have the advantages of economy and biodegradability but have also been observed to have the disadvantages of poor buoyancy characteristics, relatively low oil sorption capacity and low hydrophobicity [Choi and Cloud, 1992]. However, it has also been shown that it is possible for some natural sorbents to sorb significantly more oil than even polypropylene materials that are normally used commercially [Choi and Cloud, 1992 and Choi, 1996]. For example, Kobayashi et al. previously reported that the oil sorption of cellulosic kapok fiber used in a mat, block, band or screen was approximately 1.5–2.0 times greater than that of polypropylene mat which was observed to sorb 11.1 g B-heavy oil and 7.8 g machine oil in water. It has also been reported [Choi and Cloud 1992, Choi, 1996] That milkweed and cotton fibers sorbed significantly higher amounts of crude oil than polypropylene fiber and polypropylene web from the surface of an artificial sea water bath containing crude oil and from a crude oil bath. Milkweed was found to sorb approximately 40 g of crude oil/g of fiber at room temperature while the sorption capacity of kenaf core material for Bunker C oil was also shown to be comparable with that of polypropylene [Choi and Cloud, 1992]. These workers also demonstrated that sorbed crude oil could be recovered from the natural sorbents by simple mechanical retrieval equipment suggesting that the sorbents could be recycled several times in oil spill cleanup. Thus, the results of these workers [Choi and Cloud, 1992] suggested

that a total or partial substitution of commercial synthetic oil sorbents by natural sorbent materials could be beneficial in the oil spill cleanup operation by improving the efficiency of oil sorption and by incorporating other advantages such as biodegradability. Sun et al. [Sun et al., 2002] have also recently demonstrated that acetylation of free hydroxyl groups in rice straw with acetic anhydride without solvents provided a suitable and effective method for the preparation of rice straw acetates that have a more hydrophobic characteristic. The acetylation was performed at different reaction times and temperatures in the presence or absence of catalysts. The catalysts used were 4-Dimethylaminopyridine (DMAP), pyridine, N-methylpyrrolidine (MPI) and N-methylpyrrolidinone (MPO). DMAP was found to be the most effective catalyst used. Fourier transform infrared (FTIR) and solid state carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy were used to investigate the acetylation reaction. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were also carried out to study the thermal behavior of the acetylated rice straws. The oil sorption capacities of the acetylated straws were found by these workers to be about 16.8–24.0 g/g of acetylated straw in direct proportion to the degree of acetylation and which are much higher than those obtained previously [Choi and Cloud, 1992 and Choi, 1996] for synthetic sorbents such as polypropylene fiber. The degree of acetylation, which was measured by weight percent gain, was also observed to increase with increase in reaction time, temperature and the amount of catalyst used. It should be noted that acetylated rice straws have the advantages of low cost, high sorption capacity, high uptake rate and ease of desorption because the acetylated straw is significantly hydrophobic and does not get wet with water. The sorbed

oil can also be easily recovered from the straw by simple squeezing operation so that the sorbents can be recycled several times for oil spill cleanup. Therefore, the acetylation of rice straws and other biodegradable lignocellulosic vegetable products such as cotton, wool, sugar cane, paper, wood etc. may prove very economical, technically feasible and environmentally acceptable for applications in oil spill cleanup operations.

Oil sorption capacities of various natural and man-made fibrous sorbents were compared in a simulated seawater bath containing oil. Natural sorbents such as milkweed, kapok, cotton, and wool showed higher sorption capacities than man-made sorbents such as polyester, polypropylene, viscose rayon, nylon 6, nylon 66, and acetate. Sorption capacities of the natural sorbents were over 30 g oil/g fiber. No definite advantages were observed using man-made bicomponent and biconstituent fibers over regular man-made fibers with respect to their sorption capacity. With the exception of kenaf, all natural sorbent materials sorbed more than 30 g oil per g fiber in the simulated seawater bath. Milkweed showed the highest oil sorption among the sorbents examined. The sorption capacities decreased in the following order: milkweed > kapok > cotton > wool > kenaf. Kenaf fiber sorbed only 5.6 g oil per g fiber.

In order to study sorption mechanisms, physical configurations of these sorbents were analyzed under ESEM. It was found that the concentration of sorbed oil was greater in the twisted region of the fiber than other regions [Choi and Cloud, 1992]. Contrarily, both milkweed and kapok fibers have a rod-like structure (certain kapok fibers with flat appearance are immature fibers). Literature showed that fineness of the milkweed, kapok, and cotton fibers ranges in diameter from 20-50 μm ,

30-36 μm , and about 25 μm , respectively [Bailey, 1954, Whitford, 1954]. The micrographs substantiated that these fibers have similar fineness. Therefore, these results indicated that the fiber fineness has no significant effect in producing disparity in oil sorption capacities between milkweed and kapok vs. cotton.

The extent of lumen in these fibers is much larger than that of cotton (not shown). In addition, unlike cotton, in which the lumen is collapsed in mature cotton fibers, the lumen in milkweed and kapok does not collapse. Milkweed has a thin skin and the lumen size is almost 90% of total diameter of the fiber [Knudsen, 1990]. The lumen size for kapok is also large and is comparable to that of milkweed. Therefore, the higher oil sorption capacities of both milkweed and kapok were attributed primarily to the presence of larger, noncollapsing hollow lumens, which can increase capillary actions. Moreover, the wax content (about 3%) for milkweed and kapok as compared to cotton wax (0.4-0.8%) may explain the greater sorption capacity. The greater wax content enhances the sorbent-oil interactions through hydrophobic interaction and van der Waals forces.

In order to clarify the mechanism of oil sorption with these natural fibers, oil was applied onto the fiber surface and observed with the ESEM. A series of micrographs of milkweed fiber taken at different time intervals. The micrographs were taken after initial application of oil. A deposit of oil shown on the surface of milkweed had disappeared after 8 min. This is indicated by the clear surface of the fiber. In addition, the large deposit of oil located in the right bottom corner of the micrographs was reduced in size. All of the oil did not disappear because the volume of oil was probably too large for complete penetration into the smaller volume of the fiber lumen. Also, it is most

unlikely that the disappearance of oil was due to evaporation, since volatiles were previously removed from the oil. These results substantiate that oil sorption of milkweed is, in part, due to capillary action into its lumen. Similar phenomena were observed with cotton fibers, but this effect was not so clear as in case of milkweed fiber [Choi and cloud, 1992].

Wool is a protein fiber unlike other natural sorbent materials, which are cellulosic. This difference in chemical nature and other surface characteristics of wool could cause variation in the oil sorption mechanism. The mechanism of capillary action was not expected to be a major consideration because of the lack of lumen. Therefore, a high level of sorption capacity of wool (31.8 g oil/g fiber) suggested that there were other types of mechanisms in wool-oil interaction. Oil was spread throughout the fiber surface and covered the scaly structure. Analysis of the micrographs also revealed that more oil was observed on the cross-points of two fibers forming oil bridges between fibers, but this phenomenon was shown in all sorbent materials. Four factors could contribute to the high level of oil sorption by wool fiber: large amounts of surface wax, irregular scaly surfaces, crimp, and medulla. The first three factors suggest that adsorption, a surface phenomenon, would be the most prominent mechanism for oil sorption for the following reasons:

- 1) More adsorption is expected on the fiber surface because of the large amount of oleophilic waxes present (10-20%);
- 2) The scaly structure of wool provides large and readily accessible surface pores for oil deposits (this structure also contributes to easier formation of capillary bridges of oil between fibers);
- 3) Wool fibers grow in a wavy form with a certain amount of twist

which is characterized as crimp, and the greater surface area furnished by crimp also favors the adsorption mechanism.

4) The medulla, contributes to the absorption mechanism of oil sorbability. The medulla is a honeycomb-like structure, cells [Bergen, 1954]. This canal network through the center of the fiber provides an area for oil retention.

Kenaf is a fiber derived from the stalk of the plant whereas cotton, milkweed, and kapok are seed fibers. It contains approximately 75% cellulose and its characteristics are more wood-like. The cell wall is thick and surrounded by a bulky layer of lignin. Also, kenaf occurs in cylindrical fiber bundles rather than in single fibers. The ends of the fiber are blunt and thickened. The lumen is irregular with marked constrictions; at some points it becomes discontinuous and undefined. The fiber does not have crimp, a scaly surface, or other favorable surface characteristics necessary for oil sorption. These properties help to explain the lower oil sorption capacity of kenaf compared to the other natural fibers.

1.2. SYNTHETIC OIL SORBERS

Synthetic sorbent products can be classified in three classes: polymers, natural materials and treated cellulosic materials. The most often used polymers are polypropylene, polyethylene, polypropylene booms and polyurethane foam, which have highly oleophilic and hydrophobic properties and are the most widely used sorbents in the remediation of oil spills [Zahid et al., 1972, Schrader, 1991]. However, these materials degrade very slowly relative to mineral or vegetable products. In the case of floating polypropylene booms, it is difficult to recover all the absorbent material, the residual; nonbiodegradable material

contaminates the environment similar to the parent material [Scharder 1991].

The limitations of the above-mentioned method have led to the study of alternative methods for oil removal using biodegradable materials such as lignocellulosic fibers [Bertrand, 1993 and Anthony, 1994]. Agricultural products and residues are inexpensive and readily available. Polypropylene fiber [Sun et al., 2004] or non-woven fabrics [Radetic et al., 2003, Wei et al., 2003], melt-blown polyesters and polyurthane foam sheets have been used. But these have a serious disadvantage of bulkiness that is, inconvenient shipping and storage. To resolve these disadvantages, an oil-recovery machine was designed, which takes advantage of an on-site foaming method [Shimizu et al., 1997]. In other word, two of polyurthane liquid components are transported to the site of the oil spill, and mixing the two components produces polyurthane foams. However, this method also has difficulty in moving the on-site foaming machine to the site of oil spill, and its shipping and storage are very inconvenient [Jang and Kim, 2000].

In spite of the development of polymer for oil absorption, there have been few reports on the synthesis of ethylene-propylene-diene (EPDM) containing an aromatic moiety. Due to the non-polar hydrocarbon nature of the polymer, EPDM has excellent water resistance but poor oil resistance. An effective mean to obtain oil absorbent is to synthesize the crosslinked polymer, which does not dissolve in oil [Lu et al., 1995]. It is well known that ethylene-propylene- diene (EPDM) is an artificial rubber, which has elasticity and outstanding resistance to degradation by heat, light, oxygen, ozone, and water but poor resistance to oil.

The butyl radical of 4-tert-butylstyrene (tBS) may have some stereo effect to produce the crosslinked polymer with a large cavity in which

oil will fill. From this point of molecular design, Zhou and Cho [Zhou and Cho, 2002] prepared 4-tert-butylstyrene-EPDM-divinylbenzene (PBED) polymers by graft crosslinking polymerization of (tBS) and divinylbenzene (DVB) onto EPDM in toluene using benzoyl peroxide (BPO) as an initiator to obtain high oil absorbency. DVB is a useful crosslinking agent. The sol PBED can be reused for oil-absorption through crosslinking by ultraviolet (UV) irradiation. The effects of synthesis conditions such as solvent amount, molar ratio of DVB to tBS, EPDM content, initiator concentration, reaction temperature and reaction time were studied. The produced gels show poor gel strength after swelling in oil at high absorbency. Composite technique is one of the available methods for reinforcing them. Mechanical properties and morphologies of some composites were obtained with a tensile tester and scanning electron microscopy respectively [Zhou and Cho, 2001].

It has been known that vulcanized styrene butadiene rubber (SBR) has excellent tensile strength, tear resistance, and abrasion resistance. The graft terpolymer, tBS-SBR-DVB (PBSD) was prepared by the graft crosslinking polymerization of (tBS) and (DVB) onto unvulcanized SBR in solution process using (BPO) as an initiator to obtain high oil absorbency. The effects of synthesis conditions such as solvent amount, molar ratio of DVB to tBS, SBR content, initiator concentration, reaction temperature and reaction time on conversion, grafting efficiency, and gel fraction were examined. The swelling rates, light resistance, and tensile strength of PBSD were investigated. It was found that the tensile strength is considerably better than that of 4-tert-butylstyrene-EPDM-divinylbenzene (PBED) [Zhou and Cho 2001].

The existing oil absorbents polypropylene fiber or fabrics, melt-blown polyesters, polyurethane foam sheets, and so on, have unsatisfactory

oil- absorbing capability. What is worse, they have difficulty in shipping and storage because of their bulkiness. To overcome these disadvantages, a new concept in manufacturing oil absorbents was suggested. Prior to manufacturing, compressed sponge like materials, base materials with high oil absorption capability, were prepared by copolymerization.

Many kinds of polymers have been widely used to absorb oil spilled on water [Bertrand, 1993, Anthony, 1994]. Among them, alkyl acrylate and aromatic polymers, which have hydrophobicity and gel- type structure consisting of an elastic network and interstitial space, have been attracting much interest in the field of environment [Dong and Hoffman, 1986, Hoffman et al., 1986, Freitas and Cussler, 1987, Monji and Hoffman, 1987, Okano, 1993, Saito et al., 1993, Martel and Morcellet, 1994, Zhou and Cho, 2000, Champ et al., 2001, Sayil and Okay, 2001, Atta, 2002]. Because of hydrophobic network polymers used as absorbents for oil or some organic solvents spilled on water in the field of environment.

Jang and Kim [Jang and Kim, 2000] studied the copolymerization of styrene monomer with various long chain alkyl acrylate monomers like, 2-ethylhexyl acrylate (EHA), lauryl acrylate (LA), lauryl methacrylate (LMA) and stearyl acrylate (SA). These acrylates with long chain alkyl groups are generally known as hydrophobic materials. Therefore, a highly oil absorbing property can be obtained by controlling the composition and the crosslinking density of the copolymer. EHA, LA, and SA were chosen to evaluate the effect of hydrophobic with varying the length of alkyl groups. LMA, on the other hand, was chosen to find the difference between acrylate and methacrylate. Various crosslinked and uncrosslinked styrene /acrylate copolymers were synthesized.

Crosslinking copolymers were prepared by adding (DVB) as a crosslinking agent. At low degree of crosslinking (0.5 wt% DVB), the T_g of the crosslinked copolymers was lower than or similar to that of uncrosslinked one. Authors [Jang and Kim, 2000] conducted a detailed study on the swelling properties of the crosslinked copolymers. The influence of synthetic variables (monomer feed ratio, amount of crosslinking agent, amount of initiator, polymerization temperature, and type of acrylate monomer) of the crosslinked copolymers on the oil absorption capacity was examined. The effect of moisture was also investigated through a series of oil absorption tests.

Atta and Arndt [Atta and Arndt, 2004] synthesized new oil-absorptive polymers containing alkyl acrylate via different types of crosslinkers by chemical initiation and irradiation techniques. The copolymerization of acrylate monomers was carried out by electron-beam irradiation at different dose rates [Ichijo et al., 1994 and Makhaeva et al., 1996]. Furthermore, the crosslinking of these polymers by a high dose electron-beam irradiation in the presence of crosslinkers has been studied. They [Atta and Arndt, 2004] conducted a detailed study on the swelling properties of the crosslinked 1-octene-isodecyl acrylate copolymers. The crosslinking polymerizations were carried out in presence of different concentrations of ethylene glycol diacrylate (EGDA) and ethylene glycol dimethacrylate (EGDMA) crosslinkers via catalytic initiation and by electron beam irradiation at dose rate 80 kGy. The concentration of both crosslinkers was varied from 0.5% to 2%. The effect of various polymerization conditions (amount and types of crosslinking agent, technique of polymerization and monomer feed ratio) was studied through oil absorption test using petroleum crude oil. The oil absorbency was influenced mainly by the

degree of crosslinking and the hydrophobicity of copolymer units. The final equilibrium oil content, volume fraction of polymer and swelling capacity were determined at 293K. The effective crosslinking density (V_e), the average molecular weight between the crosslinks (M_c) and the polymer-toluene interaction parameter were determined from stress-strain measurements. The efficiencies of EGDA and EGDMA crosslinking agents towards copolymers were determined.

As mentioned earlier, synthetic sorbents such as polypropylene and polyurethane are the most commonly used commercial sorbents in oil spill cleanup due to their oleophilic and hydrophobic properties. For example, ultralight, open-cell polyurethane foams capable of absorbing 100 times their weight of oil from oil-water mixtures were previously developed by chemical modification of the matrix and adjustment of the foam structure [Jarre et al., 1979]. More recently, polypropylene was observed by Teas et al. [Teas et al., 2001] to exhibit much higher absorption capacity than (i) expanded perlite samples for light cycle oil, light gas oil and Iranian heavy crude oil and (ii) cellulosic fiber for light cycle oil and light gas oil. However, several materials such as exfoliated graphite [Toyoda et al., 1998], acetylated rice straw [Sun et al., 2002], milkweed (*Asclepias*) and cotton fibers [Choi and cloud, 1992, Choi, 1996] have been developed that exhibit much higher oil sorption capacity than polypropylene fiber (or web) or polyurethane foam. Nevertheless, it has been observed by Choi and Cloud [Choi and cloud, 1992] that the oil sorption capacity of polypropylene pad can actually be increased by blending 60% milkweed floss (which exhibited much higher sorption capacity) with 40% polypropylene in the web. Thus, these workers suggested that the blending percentage should be further optimized in terms of their performance characteristics.

However, since landfill disposal is environmentally undesirable and incineration is very expensive [Choi and cloud, 1992 and Hori et al., 2000], the non-biodegradability of these materials is a major disadvantage.

Man-made fibers have lower oil sorption capacities than the natural sorbent materials, except for kenaf. The order of decreasing sorption capacity was nylon 6, polyester > acetate > viscose rayon > polypropylene (Intersorb) > nylon 66 > polypropylene (regular) > polyethylene series (PE2, PE1, Spectra). It is known that oleophilicity is an important factor if a material is to be an effective sorbent for oil [Halligan et al., 1976]. However, oleophilicity is not a simple quantitative unit that can be measured readily. Nevertheless, by using their given chemical structures we know that all these man-made fibers are oleophilic and hydrophobic with the exception of viscose rayon.

Oleophilicity of a sorbent may be important primarily as a surface factor. It is a property which imparts an affinity of the sorbent with the oil. It also enhances wicking, which provides for easier transport of the oil along the sorbent surface and between the fibers. Rayon is a regenerated cellulosic man-made fiber which is hydrophilic. Unexpectedly, rayon sorbed almost 20 g oil per g fiber, which was even greater than the sorption capacities of certain oleophilic fibers such as nylon 66, polypropylene, and polyethylene series. In the case of rayon, the shape or physical configuration of the sorbent is probably a more important factor for retaining the sorbed oil. This is especially true in an oil-rich environment as used in the present study (40 g oil/500 mL water). In addition, a possible absorption mechanism cannot be ruled out due to the low degree of crystallinity of the rayon fibers.

A previous study pointed out that oil sorption is affected not only by

the composition of the sorbent but by its shape as well [Rankin et al., 1989]. Also, in our earlier evaluation [Choi and cloud, 1992] it was demonstrated that scoured, bleached, and extracted cotton gave good oil sorption capacity even though it was rendered hydrophilic by the chemical treatments. Therefore, the relatively high oil sorption capacity of hydrophilic fibers may be explained by molecular arrangement of the polymer and the physical configuration of the fiber such as twist, crimp, surface roughness, porosity, and fineness, especially in an oil-rich environment.

Conversely, other hydrophilic man-made fibers in this evaluation, polyvinylalcohol (PVA), acrylic with super absorbent out layer (ACR), and a copolymer of isobutylene-maleic anhydride (IBM), were not suitable as sorbent materials in the simulated seawater bath. PVA and ACR even submerged under the surface of the oil slick into the water and sorbed a large amount of water. This caused considerable fiber swelling. Swelling of the IBM fiber was probably due to hydrolysis of anhydride groups in the fiber. However, when these highly hydrophilic fibers were used in a 100% oil bath, PVA, ACR, and IBM sorbed 30.7, 27.8, and 7.3 g oil per g fiber, respectively. These results again substantiated the importance of fiber structure in oil sorption. Nevertheless, hydrophilic fibers such as rayon, Intersorb polypropylene, PVA, ACR, and IBM would not be applicable in a practical cleanup of oil spills on water surface, because they would become saturated by water before contacting oil. Other environmental factors such as waves, wind, etc., could multiply such problems. The oil sorption capacity was substantially different in nylon 6 and nylon 66 fibers which have similar chemical structures but differ in their molecular arrangements.

Both nylons have the same fineness and they also have crimps and similar lengths. Therefore, variation in oil sorption capacity may be due to the difference in molecular arrangements. However, a further study is necessary to elicit more detailed information. Three different polyethylene fibers were evaluated. PE1 and PE2 contain 5-10% of 1-octene copolymer. Their finenesses are essentially the same, and PE2 is only slightly longer than PE1. Spectra fiber is a very highly oriented polyethylene fiber [Borman, 1989]. Oil sorption of Spectra fiber was less than any of the man-made fibers evaluated. This was attributed mainly to two factors: the larger denier of Spectra fiber and its compact molecular arrangement due to a high degree of crystallinity and orientation. Therefore, the latter tends to suggest that the oil sorption of some man-made fibers involves the absorption mechanism, which can be varied by the molecular arrangement of the fiber.

Polypropylene fiber is one of the most commonly used sorbents in oil spill cleanup because of its oleophilic and hydrophobic characteristics [Schatzberg, 1971]. However, natural and biodegradable sorbents such as cotton, milkweed, and kapok offer distinct advantages and have been investigated in previous studies [Halligan et al., 1976, Kobayashi et al., 1977 and Choi and Cloud, 1992].

Crosslinked water born reactive polymer system has been developed to provide enhanced specific adhesion to plastic film. The system combines low activation temperatures with high solvent and heat resistance. Crosslinked efficiency is evaluated in terms of solvent resistance, softening point and tensile strength and elongation [Lombardi et al, 1987]. Sambasivam et al. [Sambasivam et al., 1996] developed new formulations based on proprietary epoxies to apply in microelectronic packaging applications. The features of these

formulations are short cure cycle, long term stability at 25 °C, very low cure volatile, low moisture absorption, low coefficient of thermal expansion (CTE) and excellent adhesion to various substrates.

Crosslinking modification of two woven (35/65 polyester / cotton and 100% cotton) fabrics and (90/10 cotton /Lycra) can improve esthetics and functional properties. The two woven fibers were treated with two different DMDHEU resins (one unalkylated and the other a blend of alkylated/unalkylated DMDHEU of low formaldehyde content) and poly ethylene glycol 1,000 solutions. Curing under selective mild conditions produced modified fabrics (containing crosslinked polyols). All treated fabrics have good thermal storage and release properties, enhanced absorbency, flex life, antistatic behavior, and oil soil release than untreated fabrics when the blended resin was used in the crosslinking formulation.. The treated cotton/polyester fabrics had the additional benefit of high strength retention, toughness, and elongation. Photomicrographs show that the crosslinked polymer protects both cotton and synthetic fibers from flexural failure. [Vigo et al., 1991]. Fujita et al. [Fujita and Soane 1988] prepared crosslinked membrane with controlled pore size distribution. Membrane reactors are recognized as possessing some unique capabilities [Tundo, 1991]. The three most significant are :

- Reactants and products can be transported from the catalyst by convection, which is more efficient than the diffusion process which control transport of the compounds in conventional supports
- Membranes can compartmentalize the reactor, providing an interface for a second process stream
- In multi-layer composites, membrane can provide highly selective control over reactant flux.

The limitation is presently that polymer materials generally tolerate only relatively mild reaction temperatures. Hollow fibers are frequently used in membrane reactors when minimal reactor volume is desired. The main drawback is that they are extremely sensitive to fouling and clogging caused by particles in the feed stream [Cabasso, 1987].

1.3 MINERAL PRODUCTS AS OIL SORBERS

α -Silica Aerogels

Aerogels are nanoporous materials made by a sol-gel process followed by drying at supercritical conditions. They are solid metal-oxides with open foam-type structures which allow penetration of various sizes of compounds into the solid. The combination of the solgel and supercritical drying techniques used for the synthesis of these materials impart into them unique properties such as large surface areas (up to 1000 m²/g and greater), high porosity, low density and low thermal conductivity [Lee et al., 1995, Hrubesh et al., 1999 and Reynolds et al., 2001]. Various applications such as thermal insulation, support of catalysts, supercapacitors for electric cars, microfilters, adsorbents, controlled release of drugs, inert confinement fusion, etc. of these materials have been investigated [Fricke, 1988 and Lee et al., 1995]. Since the first synthesis of aerogels from water glass [Kistler, 1931], there has been significant advancement in the preparation methods of aerogels. For example, the introduction of alkoxide eliminated the tedious washing and solvent exchange steps, thus greatly accelerating the process [Nicolaon and Teichner, 1968]. In spite of the fascinating properties of silica aerogels, there are some problems that need to be addressed before their commercialisation can be fully realised. One major obstacle to their commercialization is the collapse of their

structure due to adsorption of water. Substitution of alcohol with CO₂ supercritical drying is desirable because CO₂ is more economical, safer to use since it is non-flammable, non-explosive and chemically inert in the conditions it is employed and has a low critical temperature. However, aerogels produced by CO₂ supercritical drying have another significant problem of low hydrophobicity unlike the aerogels produced by alcohol supercritical drying that have hydrophobicity caused by the presence of alkoxy substituents on the silica matrix. Nevertheless, this hydrophobicity is not permanent because alkoxy substituents can be hydrolysed by moisture or water. Recently, Schwertfeger et al. [Schwertfeger et al., 1992] prepared hydrophobic aerogels by mixing MeSi(OMe)₃ with tetramethoxysilane (TMOS). However, these workers reported that these aerogels had a tendency to shrink during supercritical drying and that the transparency of the aerogels decreased with an increase in MeSi(OMe)₃ [Schwertfeger et al., 1992]. More recently, Yokogawa and Yokoyama [Yokogawa and Yokoyama, 1995] reported the successful preparation of very low density trimethylsilyl (TMS) modified silica aerogel that was more hydrophobic than conventional aerogels even by using the CO₂ supercritical drying process. The TMS modified aerogel was reported to maintain initial properties such as transparency, density and size even after the moisture-resistance test [Yokogawa and Yokoyama, 1995]. The modified aerogel also exhibited the same transparency as conventional aerogels as well as a very small shrinkage ratio during the supercritical drying. The workers used infrared, ¹³C nuclear magnetic resonance (NMR) and ²⁹Si NMR to observe the existence of TMS in the aerogel [Yokogawa and Yokoyama, 1995]. Tillotson and Hrubesh previously described a two step synthesis to produce a sample with a

very low density of 0.003 g/cm^3 and better transparency than conventional aerogel produced by a single step [Tillotson and Hrubesh, 1992]. However, this two-step synthesis of Tillotson and Hrubesh requires a complete removal of alcohol after the synthesis of partially condensed silica precursors. The second stage involves the formation of a gel under basic conditions in the presence of additional water. Subsequently, Lee et al. [Lee et al., 1995] described the synthesis of low-density, hydrophobic aerogels involving the two-step synthesis, supercritical drying with liquid carbon dioxide and surface modification by vapour-phase methoxylation with methanol vapour. These workers [Lee et al., 1995] reported that there was need to remove alcohol after oligomer synthesis in order to obtain aerogels of high transmittance and that aerogels having a density of 0.034 g/cm^3 could be produced without removal of alcohol. Lee et al. [Lee et al., 1995] used scanning electron microscopy (SEM) to observe the microstructure of the aerogels and Fourier transform infrared (FTIR), thermo-gravimetry analysis (TGA) and Brunauer, Emmett and Teller analysis (BET) were used to investigate the surface properties. UV-VIS spectroscopy was used to measure the transmission of light. The BET surface area was found to be in the range of $750\text{--}870 \text{ m}^2/\text{g}$ for aerogel densities of $0.05\text{--}0.2 \text{ g/cm}^3$. Other workers [Lu et al., 1996] have also reported modification of aerogels by incorporation of chemical functionality in order to yield materials that are hydrophobic. In this regard, the perfluoro functional group has been found to exhibit excellent properties [Falk and Mueller, 1981] and has been incorporated into silica aerogels [Hrubesh et al., 2001] to produce a durable hydrophobic material that is useful for separation of organic materials from mixtures of organics and water. Hrubesh and co-workers

[Hrubesh et al., 2001] showed that the adsorption capacity of the CF_3 -modified silica aerogels for various organic solvents exceeded the capacity of comparable granular activated carbon (GAC), on a gram-per-gram basis, for all the solvents tested. The improved performance of adsorption capacity by the aerogel over GAC was found by these workers [Hrubesh et al., 2001]. Reynolds et al. [Reynolds et al., 2001] recently presented a report on the intrinsic oil absorbing properties of a CF_3 -functionalized aerogel which was synthesized by the hydrolysis-condensation of tetramethylorthosilicate, $(\text{CH}_3\text{O})_4\text{Si}$ and (3,3,3-trifluoropropyl)-trimethoxysilane, $\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, in CH_3OH by NH_4OH and H_2O catalysed reaction, followed by supercritical CH_3OH drying. This material was found to exhibit the following properties in simulated oil-spill cleanup conditions:

- Completely absorbs oil at oil/aerogel ratios of up to 3.5, producing a dry solid when separated from the water,
- forms an emulsion at oil/aerogel ratios of 4.6–14, which is easily separated from the water,
- absorbs only part of the oil at oil/aerogel ratios of 16 and greater, with free-phase oil being observed,
- is extractable and reusable for at least two times additionally,
- absorbs oil 40–140 times better than the nonfunctionalised silica aerogel,
- has a higher oil absorbing capacity when in a nonpowder form, and
- performs equally well with two different crude oils.

In their report, Reynolds et al. also showed that the CF_3 -functionalised aerogel compared very well with some absorbing materials that have previously been developed and tested for removal of oil spills. Some of the materials are used directly as powders while some are used as

coatings on devices that aid in the absorption and separation of the oil. Since the non-powder forms of CF_3 -functionalised aerogel were found to perform much better than the powder form for absorbing capacity and some absorbing materials that are designed into devices have been found to exhibit enhanced absorption capacity, it was therefore suggested by these workers [Reynolds et al., 2001] that CF_3 -functionalised aerogels might perform much better if they are used as coatings on devices.

Subsequent report by Reynolds and his co-workers [Coronado et al., 2001] indicated successful synthesis of CF_3 -aerogels using $(\text{CH}_3\text{O})_4\text{Si}$ and nominally 30, 10 and 1.5 mol% of $\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ in a NH_4OH catalysed reaction followed by supercritical extraction with CH_3OH . These workers characterised the aerogels by IR, surface areas, relative pore size distributions and decomposition behaviour. Water absorption and sessile drop experiments showed that the aerogels were hydrophobic. The water absorption experiments were conducted by exposing them to a water-saturated air atmosphere at 20°C and measuring the water absorption by weight gain. The IR showed that the $\text{CF}_3(\text{CH}_2)_2$ - group was intact after the gelation process and following the supercritical drying. Decreasing amounts of Si- OH groups were also obtained in all cases with increase in the amounts of $\text{CF}_3(\text{CH}_2)_2$ -group. The aerogels decomposed on heating in air and the transition from hydrophobic to hydrophilic appeared around 375 – 400°C which corresponded to the disappearance of the $\text{CF}_3(\text{CH}_2)_2$ - moiety bands in the IR. Their oil absorption results showed that the absorption capacity of the CF_3 -aerogels at an oil/aerogel ratio of 3.5 was independent of the concentration of the $\text{CF}_3(\text{CH}_2)_2$ - group implying that they can actually absorb oil as much as 237 times their weight, much more than

previously obtained [Toyoda et al., 1998 and Reynolds et al., 2001]. The CF₃-modified aerogels may therefore be very useful, especially when they are further integrated into devices, for oil-spill cleanup applications. It has actually just been demonstrated by Coronado et al. [Coronado et al., 2002] that a device formed by incorporating such hydrophobic CF₃-modified aerogel into any commercially available solid support materials like fibreglass, alumina, insulation, alumina tiles, dacron and cotton wool, and vitreous carbon foam are quite effective in selectively absorbing oil in the presence of water, thus providing an efficient method for oil spill recovery.

b-Zeolites

In the past few years, research is increasingly focusing on hydrophobic pure-silica (or high silica) zeolites as alternative sorbents for activated charcoal for sorption of organic pollutants (such as volatile organic compounds). Such pollutants are routinely removed by sorption on activated carbon [Ruhl, 1993, Ruddy, 1993 and Stenzel, 1993]. Hydrophobic zeolites have a small percentage of aluminium atoms in their crystal structure thereby shifting their adsorption affinity away from polar molecules, like water, towards nonpolar substances, like organic solvents (i.e. they are highly organophilic). These zeolites are thermally and hydrothermally stable up to about 1300°C [Maesen and Marcus, 2001] and like other classic aluminosilicates, they have a unit structure with a defined pore size of 0.2–0.9 nm, resulting in a high specific surface area [Breck, 1974]. Hydrophobic zeolites also have the following advantages over active carbon sorbents:

- Little need for safety equipment with regards to fire risk since zeolites are inflammable.

- Co-adsorption with water possible only when the relative humidities are higher than 70% compared with 50% for active carbon.
- Can be regenerated with steam [Ham et al., 1999 and Kuntzel et al., 1999] or by calcinations at high temperatures [Otten et al., 1992 and Ruthven, 1988]. One disadvantage of the hydrophobic zeolites is, however, their much less adsorption capacity for most organic components in comparison with active carbon sorbents [Kuntzel et al., 1999].

Hydrophobic high-silica or pure silica zeolites are commonly synthesised either by direct synthesis or by thermochemical framework modification of hydrophilic zeolites through dealumination procedures [Maesen and Marcus, 2001 and Jansen, 2001]. Many dealumination processes have been developed over the years such as steaming [Loiseau and Ferey, 1996 and Campbell et al., 1996], treatment with mineral or organic acids [Barrer and Makki, 1964 and Jones et al., 2001], or chelating agents [Kerr, 1968], reaction with silicon tetrachloride [Beyer and Belenykaja, 1980 and Barthomeuf, 1994] and treatment with silicon hexafluoride [Skeels and Breck, 1984 and Ferey 1998]. The surface properties of zeolites have also been modified by silylation to produce hydrophobic zeolites [Huang et al., 1993 and Zhao and Lu, 1998]. Various silylating agents that have been used to modify zeolite surfaces include alkylchlorosilanes, and aminosilanes. A review of the procedures for silylation of silica with various silylating agents has been presented [Van Der Voort and Vansant, 1996].

Chen [Chen, 1976] was the first to propose the use of hydrophobic molecular sieves to remove organics from water. Recently, hydrophobic zeolites have also been reported [Zhao et al., 1998 and

Meininghaus and Prins, 2000] to have the ability to remove volatile organic compounds. More importantly, some other workers have recently published the results of their work on the application of zeolites for oil-absorption from oil-water mixtures [**Andras et al., 1997**]. It is interesting to note that high-quality zeolites with high water- and oil absorption, and cation exchange capacity may be readily produced from inexpensive fly ash (a by-product of coal and power stations) and other solid waste materials containing silica and alumina thus, providing a solution to other environmental problems in addition to application in the removal of oil spills. Some researchers from Spain have actually recently reported their work on synthesis of zeolites from fly ash at pilot scale and the applications of these materials in waste water treatment technology [**Querol et al., 2001**]. Further development of hydrophobic and organophilic zeolites including those prepared from fly ashes and wastes from aluminium refining may therefore find excellent application in oil spill cleanup operation. Geopolymers which are amorphous to semi-crystalline three-dimensional silico-aluminate structures similar to aluminosilicate zeolitic structures have surface areas of 1 to 2 orders of magnitude higher than that of zeolites and high thermal stability (up to 1000–1200°C) [**Davidovits, 1991**]. Modification of geopolymers to make them hydrophobic may therefore also produce excellent materials for oil spill remediation. Like zeolites, geopolymers can also be prepared cheaply from a wide variety of industrial aluminium and silicon-rich waste materials such as fly-ash, contaminated soil, mine tailings and buildingwaste as well from clay materials such as kaolinite and metakaolinite [**Davidovits, 1991, Phair et al., 2000, Xu and Van Deventer, 2000, Swanepoel and Strydom, 2002 and Xu et al., 2002**]

c- Organophilic Clays

Clay minerals consist of small crystalline particles that are formed from silica tetrahedral sheets (with a silicon ion tetrahedrally coordinated to four oxygen atoms) and aluminium or magnesium octahedral sheet (where an aluminium or magnesium ion is octahedrally coordinated to six oxygens or hydroxyls) [Grim, 1968]. Clay minerals may attain a net negative charge by isomorphous substitution of silicon ion for aluminium ion in the tetrahedral layers or similar substitution of aluminium ion for magnesium, manganese and other cations of similar size in the octahedral layer. Thus, cations like sodium, potassium and calcium, known as exchangeable cations, may then be attracted to the mineral surface to neutralise the layer charge. These exchangeable cations may then readily be further replaced in the soil by other cations such as inorganic and metallic cations from wastes. Nevertheless, it has also been previously observed by Theng [Theng, 1974] and Raussell-Colom and Serratos [Raussell-Colom and Serratos, 1987] that many polar organics (e.g. alcohols, amines and ketones) are adsorbed into the external clay surface, interlayer space and probably on clay particle edges by electrostatic attraction and ion exchange reactions. Ding et al. [Ding et al., 2001] also indicated in their review that clay minerals such as smectites and pillared interlayer clays (PILCs) have found applications as adsorbents for organic compounds in liquid phase and in the controlled release of agrochemicals.

The synthesis of such materials has been previously reviewed by Kloprogge [Kloprogge, 1998]. However, clay minerals still have greater tendency to adsorb inorganic cations in wastes than the organic constituents. This is due to the usually larger molecular size of the organic compounds and the hydrophilic nature of clays that allows the

covering of the clay surfaces by highly polar water molecules thereby reducing the attraction of poor water-soluble organic species [Chiou et al., 1983]. There is therefore great need for the hydrophobicity and the interlamellar distance of clay minerals to be increased in order to enhance their organophilicity. It has been demonstrated by Boyd et al. [Boyd et al., 1988], McBride et al. [McBride et al., 1977] and Evans and Pancoski [Evans and Pancoski, 1989] that quaternary ammonium cations such as hexadecyltrimethyl ammonium (HDTMA) interact with clays and replace the exchangeable inorganic cations on their surfaces, thus forming a stationary phase in the clay particles. Furthermore, due to the larger size of the HDTMA cations than the replaced cations, the interlamellar distance (basal spacing) of the mineral increases and additional space is produced in the particles thus facilitating the sorption of other organic compounds. In other words, the minerals adsorb fewer water molecules and they are changed from being hydrophilic to being organophilic. Such clay minerals that have been modified with quaternary amine cations replacing the exchangeable inorganic sodium, potassium or calcium on the clay surface are known as organoclays.

The most commonly used quaternary amine is the dimethyl (dihydrogenated) tallow ammonium type which may include a benzyl molecule if the application requires it. By choosing such a long-chain quaternary amine (12–18 carbon atoms) for the modification, the clay will swell in organic fluids such as diesel and jet fuel, gasoline, kerosene and others [Alther et al., 1988]. It should be noted too that clays are porous and have high surface areas. Clays, particularly organoclays, are therefore potential candidates for application in oil spill cleanup operations. Gitipour et al. have actually used sorption

isotherms and column leach tests to show that bentonite clays modified with dimethyl di(hydrogenated) tallow effectively removed aromatics from oily liquid wastes [Gitipour et al., 1997]. Their X-ray diffraction analyses also indicated increases in the basal spacing of the modified bentonite as a result of the interaction between the clay and organics. More recently, Moazed and Viraraghavan [Moazed and Viraraghavan, 1999, 2001 and 2002] investigated the potential of powdered bentonite organoclays in the removal of oil from oil-in-water emulsions. Granular organoclays have also been observed by Alther [Alther, 1995 and 2002] to be more effective than activated carbon in removing a wide variety of oil from water because they do not experience the problem of blinding of pores normally experienced by activated carbon. According to this worker, granular organoclay can be seven times more effective than activated carbon, depending on the kind of oil being removed from the waste water. Alther's data illustrate the effectiveness of powdered, non-ionic organoclays for removal of various mineral oils from water. The data for activated carbon for removal of turpentine is included for comparison. Furthermore, Alther has also demonstrated in other reports [Alther, 2001 and 2002] that organoclays can be used to improve the adsorption efficiency of activated carbon, thus lowering the operation costs associated with carbon even if there is no oil, or only a very small amount is present in the water. Moazed and Viraraghavan [Moazed and Viraraghavan, 2001 and 2002] have reported too the use of a granular bentonite organoclay/anthracite mixture in filtration application to treat representative oil-in-water emulsions. An hydrophobic, iron-containing clay material that is magnetic has also been previously reported by Bryk and Yakovenko [Bryk and Yakovenko, 1987] to be suitable for

the cleanup of petroleum spills on water. These workers observed that the material floats on water, have a petroleum adsorption capacity of 3.5–4.0 g petroleum/g sorbent and can be regenerated. More recently, the synthesis of magnetic clay composites based on the adsorption of magnetite and Co ferrite magnetic nanoparticles onto the external surface of a Na-saturated clay mineral was reported [Bourlinos et al., 2002]. These magnetic solids which, according to the report, can be converted easily to organoclays and other valuable derivatives through ion-exchange reactions, were characterized by XRD, EPR, Mossbauer, magnetic measurement and TEM.

d- Other Mineral Products

Other mineral products that have been investigated for application in oil sorption include exfoliated graphite, expanded perlite and activated carbon. The results obtained by Teas et al. [Teas et al., 2001] showed that some commercial types of hydrophobic perlite had absorption capacity comparable to natural and synthetic organic materials used for oil spill cleanup applications. These workers then suggested that the enhancement of the hydrophobic properties of perlite could result in better performance in a water bath and that the nature of spilled oil appeared to play an important role in the selection of the proper absorbing material. They further suggested that the substitution of mineral materials for commercial synthetic sorbents that are widely produced in Greece for oil spill cleanup operations is possible, especially as they are friendly to the environment and abundantly available locally. Exfoliated graphite was reported too to sorb [Toyoda et al., 1998 and 1999] heavy oil floating on water and separate it easily from the water. The exfoliated graphite was found to have a maximum

A-grade heavy oil sorption capacity of more than 80 g oil/g graphite. It was observed too that by simple compression, up to 80% of the heavy oil sorbed into the exfoliated graphite could be recovered. However, the following suggestions for further investigation were made for the development of better exfoliated graphite materials for the sorption and recovery of heavy oil dispersed into water, particularly seawater:

- Quantitative studies on sorption capacity and rate of different grades of heavy oils,
- Development of a simple way to manipulate exfoliated graphite because it is very light and bulky,
- Properties of exfoliated graphite required for obtaining a high sorption capacity,
- Mechanism of sorption of heavy oils by exfoliated graphite in order to discover the most appropriate exfoliation conditions of graphite, and
- Development of effective and practical techniques to recover heavy oil sorbed into graphite and recycle both recovered oil and exfoliated graphite.

Thus, these workers have subsequently carried out a series of further investigation on (i) the recovery of spilled or dispersed heavy oils using carbon materials and (ii) the recycling of both heavy oils and carbon materials. Their promising results on exfoliated graphite have been published in various articles [Inagaki et al., 1999, Toyoda et al., 1999, Toyoda and Inagaki, 2000 and Tryba et al., 2000]. They have also presented a review [Inagaki et al., 2001] of their experimental results on sorption capacity of a number of exfoliated graphite samples with different bulk densities, the recovery of heavy oil from, and the recycling performance of, exfoliated graphite samples. This review indicates that exfoliated graphite has much higher heavy oil sorption

capacity than polypropylene mats and natural fiber component of cotton, milkweed and kenaf. The review also shows that fir fibers, which are also fiber component of wasted fir tree carbonized up to 900°C, exhibit comparable sorption capacity for both A- and C-grade heavy oil.

As mentioned earlier under the discussion on zeolites, activated carbon has been widely used for the adsorption of organics, particularly for removal of volatile organic compounds. The advantages of activated carbon include the fact that they are rather cheap and readily available from many companies and they have high initial adsorption capacities. However, it has been observed that activated carbon has several disadvantages [Fajula et al., 1994] such as fire risk, pore clog (due to polymerization of some VOCs catalysed by ashes present on activated carbon surfaces), hygroscopicity and some problems associated with regeneration, etc. Nevertheless, as already discussed in the section of organoclays, the oil adsorption capacity of activated carbon can be significantly improved by using organoclays/activated carbon mixtures. Thus, it is suggested that mixtures of activated carbon and other porous sorbents such as hydrophobic silica aerogels, zeolites and geopolymers may also be useful for oil sorption and recovery.

1.4 CHARACTERIZATION OF OIL SORBERS

The controlling mechanism of oil sorption by the sorbents could be absorption, adsorption, capillary action, or a combination of these. [Zahid et al., 1972] postulated that absorption probably was not a significant effect in sorption of oil in polypropylene fibers because of their high crystallinity. It was claimed that the capillary bridges in the voids between the filaments were the main controlling mechanism. On

the other hand, the mechanism to sorb oil by some natural fibers, such as cotton and milkweed, was attributed to their surface wax and hollow lumens [Choi and Cloud, 1992 and Johnson et al., 1973]. The sorption of oil by a particular material is a complex phenomenon. The rate and extent at which oil is sorbed into the sorbent system are mainly dependent upon the chemical nature of the sorbent, the amount of surface wax, the molecular arrangement of the polymer, and the physical configuration of the fiber such as hollow lumen, twist, crimp, surface roughness, porosity, and fineness. Factors such as the chemical nature of the sorbent and the surface wax determine oleophilicity and surface energy of the sorbent. These are important properties in the absorption and adsorption mechanisms. The molecular arrangement of the polymer within the fiber structure is also a main factor in the absorption mechanism. On the other hand, the physical configuration of the sorbent is a more important property for adsorption and capillary action. Because of the complexity of the sorption process and the unique characteristics of any particular sorbent, it is important that each material be evaluated to determine its mechanism of sorption.

In previous study, cotton and polypropylene fibers which were structured into nonwoven matrices showed different sorption mechanisms when they were observed under the environmental scanning electron microscope (ESEM) [Choi et al., 1992]. The use of the ESEM and the determination of oil sorption capacities are techniques that can provide insight as to the proficiency of a fiber to sorb oil in a cleanup operation. This provided the basis to study other materials for their sorption mechanisms by ESEM. This technique had never been used for this type of evaluation. Therefore, the purpose of the study was to investigate sorption mechanisms of various other

fibers. The sorption of oil into these fibers was directly observed through the ESEM. Sorption capacity measurements were also conducted in a simulated seawater bath to determine the potential of these fibers for use in oil spill cleanup operations. Analyses of sorption mechanisms using an environmental scanning electron microscope revealed that an oil deposit disappeared from the fiber surface after a certain time interval in milkweed, kapok, and cotton. This suggested that the sorption of oil in these fibers occurred through capillary action, probably due to their hollow lumens. Contrarily, adsorption, a surface phenomenon, would be the most prominent mechanism for oil sorption of wool fibers due to large amounts of surface wax, irregular scaly surfaces, and crimp. Effects of both adsorption and absorption were shown in the oil sorption of man-made fibers, depending upon the type and shape of the sorbent. Dumb-bell like oil deposits were seen on the fiber surface in certain oleophilic man-made fibers, because of a partial wetting of oil on the fiber surface. For some hydrophilic man-made fibers such as polyvinylalcohol and copolymer of isobutylene-maleic anhydride, the physical configuration of the fiber was a decisive factor in determining oil sorption capacity of the sorbents.

When a crosslinked polymer is placed in a liquid, which is a solvent for the uncrosslinked polymer, it swells to an extent, which is dependent upon the interaction between the polymer and the solvent, and it is depend on:

1. Swelling potential
2. The elastic potential (which is determined by the crosslink density).

Equilibrium is reached when these two potentials, which act in opposite directions, are equal (the increase of elastic energy of the chains

forming the network balances the decrease in the free energy consequent to mixing of polymer segments with solvent molecules). This leads to the well-known Flory equation [Flory and Rehner, 1943]:

$$\frac{1}{M_c} = - \frac{2}{M_0} \frac{(\bar{v} / V_1) [\ln(1 - v_s) + v_s + \chi v_s^2]}{[v_s^{1/3} - \frac{1}{2} v_s]}$$

Where:

M_c is the number-average molecular weight of a network chain,

M_0 is the number-average molecular weight of a network primary chain (a primary chain is in the linear molecule before crosslinking),

\bar{v} is the specific volume of polymer.

V_1 is the molar volume of the solvent,

Φ_p is the final swollen equilibrium polymer volume fraction,

χ is the Flory polymer- solvent interaction parameter

The Flory interaction parameter χ is a measure of the interaction between any given solvent and a given polymer. It is a free-energy parameter and contains both enthalpy and entropy terms. It is also a temperature-dependant quantity and is also concentration dependant over a wide range of polymer concentrations. The parameter χ must be measured for every polymer-solvent pair. It can be calculated by different methods. Among these methods, equilibrium swelling [Mullins, 1959, Manjarai et al., 1963 and Biskup and Cantow, 1973], osmotic pressure [Okazwa and Kaneko, 1971, Sugamiya et

al., 1974], vapor pressure [Allen et al., 1964, Okamoto and Overberger, 1974], sedimentation-equilibrium ultracentrifugation [Chu and Munk, 1977], viscosity [Bristow and Watson, 1958, Cowie, 1969], optical studies [Ammon et al., 1965, Desphande et al., 1974, 1978] and inverse gas chromatography [Reese and Tucker, 1965, Tait and Abushihada, 1977 and Galin and Rupprecht, 1978].

The value of the swelling equilibrium is related to the nature of the polymer solvent system and provides information concerning the nature of the crosslinking and reinforcement. In order to determine the final swollen equilibrium and polymer volume fraction (in percent), it is necessary to place a sample of known density in the chosen solvent until weight measurements indicate the saturation of the polymer by liquid. Assuming that no extractable are present, and that all the absorbed solvent causes swelling.

polymer volume fraction (ϕ_p) is given by:

$$\phi_p = \frac{(W_1 - W_0) \rho_p}{W_0 \rho_s} \times 100 \quad (1.9)$$

Where

W_0 is the sample weight before swelling ,

W_1 is the sample weight after swelling,

ρ_p is the density of polymer sample,

ρ_s is the density of the solvent.

In order to obtain the curve of swelling rate, it is necessary to make a series of gravimetric measurements and determine the percentage volume swelling or weight increase as a function of time. Accurate determination of the swelling-time relationship requires a large number of experimental measurements, especially in the early stages of

swelling, the gravimetric method usually requires an interruption of the swelling process, and this involves experimental difficulties. The accuracy of data obtained by this method is low. Sol-gel analysis is carried out by soaking polymer sample in a solvent at constant temperature for a given time (from minutes up to hundreds of hours). After the soaking, the gel is obtained by drying the residual sample in vacuum at room temperature. The sol is determined as the difference in weight before and after the swelling experiments.

The sol fraction (in percent) is expressed by :

$$\text{Sol fraction} = \frac{\text{Sol}}{\text{Sol} + \text{Gel}} \times 100 \quad (1.10)$$

Goiti et al. [Goiti et al., 2004] study some properties of networks produced by the Diels-Alder reaction between poly (styrene-co furfuryl methacrylate) and poly (styrene-co furfuryl methacrylate) networks. The resultant crosslinked polymers were swollen to equilibrium in toluene at 25 °C and swelling properties measured by gravimetric and dimensional measurements. The swelling behavior of these organogels is dependant on the composition of the copolymer and the concentration of bismaleimide.

Crosslinked polymers are important in chemical research and practice owing to a wide rang of applications. Chemical resistance water treatment, chromatographic techniques, biomedical and biochemical applications, solid phase organic synthesis, enzyme immobilization soil conditioning, solvent, ion separation, organic coating and oil sorber are using crosslinked polymers as the principal substrate. Crosslinked polymer networks are excellent materials for multiple applications [Malik and Clarson, 2002].

Crosslinked reactive polymers with novel structures have been prepared from the corresponding monomers or by newly developed chemical modification reaction. These include the preparation of polymers with two or three carbon spacer groups between backbone and crosslinkers. Novel applications of these polymers in asymmetric synthesis, pregnable polymeric protecting groups, supernucleophilic catalysts, polymeric separation media for HPLC, as well as aids in the determination reaction mechanisms have been investigated [Frechet et al., 1987]. Microenvironment effects within the polymer beads are shown to be important when considering the use of an insoluble reactive polymer.

1.5 METHODS USED TO CONTROL OIL SPILL

Transportation of petroleum from oil fields to consumers may require 10 to 15 transfers. Tankers, pipelines, trains transport petroleum, and tank trucks stored temporarily in a cultivator of facilities. Accidents may occur during each of these transportation and storage steps [Fingas et al. 1979]. Offshore and shoreline waters can be polluted by runoff from offshore oil exploration, production and spills from ship transport of oil. Water can be polluted by runoff from oil fields and refinery areas and, in some cases process effluent from petroleum and petrochemical plants [Johnson et al. 1973]. Under favorable conditions, oil in a clean water body may continue to spread over the water surface and form a monomolecular layer. The oil film on the surface of water impairs the exchange of energy, heat, moisture, and gases between the water reservoir and the atmosphere [Pushkarev et al., 1983]. Crude oil consists of different hydrocarbons that range from a light gas (methane) to heavy solids. The most important and prevalent

elements in petroleum are hydrogen and carbon. Which comprise up to 98% of some crude oils and 100% of many refinery products. Other constituents of petroleum are hydrocarbon derivatives containing oxygen, sulfur and nitrogen, and inorganic metals such as vanadium, nickel and mineral salts [Fingas et al. 1979]. When oil is spilled on water or on land, the physical and chemical properties of oil change progressively. This process is referred to as weathering. The volatile components evaporate quickly. Some of the medium-sized polycyclic aromatic hydrocarbons are slightly soluble. Some of the products, which are degraded by sun and microorganisms, are highly soluble. Weathering rates are not constant but are usually highest in the first few hours. Major processes of weathering of oil spilled on water include evaporation, dissolution, oxidation, emulsification, and microbial degradation. If the residue oil is adsorbed to other material of high specific gravity such as silt or clay suspended in the water. The specific gravity of the residual may exceed 1.0 and sink. The residue continues to spread from an area of dense saline water to less dense freshwater and may then sink. In the case of crude oil evaporation plays an extremely important role in its volumetric loss after a spill. It was reported that 25% of the total volume of spilled crude may be evaporated within one day. Gasoline loses about 50% of its original volume within 7 to 8 min at 20 °C [Fingas et al. 1979]. [Galt et al. 1991].

The spilled oil contributes an undesirable taste and odor to drinking water and causes severe environmental damage [Blumer, 1969]. Contaminated water cannot be used for municipal water supply, for industry, nor for irrigation [Blumer, 1969, Morita et al., 1987]. Public concern for sustaining a healthy environment has resulted in stronger

environmental regulations regarding water quality and use of hazardous chemicals and substances. This concern has resulted in the need for improved techniques and methods for the use and reuse of hazardous chemicals and for remedial measures where contacts with the environment occur. Improved techniques for control and removal of oil slicks is one area of research under active development. Naturally cleaned oil spill, allow oil to be degraded and removed by natural means, takes long time to be fully effective. Oil dispersant or an oil-sinking agent can enhance this method. Oil gelling act as a surface-tension modifier, coagulating the spilt oil, and enhance the potential for mechanical removal techniques, for example recovery of solidified oil with a net. In both cases, there is disadvantage that the spilt oil cannot be reused. Therefore, recent trials of spilt oil treatment have been focused on oil absorbents.

1.5.1 Mechanical Recovery of oil spill

Mechanical recovery is the transfer of oil from the spilled area to some transportable temporary storage by the help of oil-booms or skimmers. Oil booms are floating barriers, used to prevent spreading of oil on water, and sometimes to thicken the layer of oil by reducing the area into which it has spread [Milgram, 1977, Bellier and Mossarte, 1979 and Greene et al., 1979]. Oil skimmer is a mechanical pick up device, which physically removes oil from the seawater surface. It contains three basic components: the pickup head, the pump system, and the oil water separator.

Various types of skimmers are available, most of which rely on the ability to physically skim the oil off the water surface, to adhere the oil to a solid surface, or to absorb it into a porous material.

a-Adhesive surface devices:

This group of oil recovery units relies on the adhesion of oil to a solid surface. This type employing a rotating drum or cylinder covered with oil absorbent materials that have ability to absorb the oil from an oil and water mixture. Oil adheres to the drum can scraped off the surface by a knife blade or by rollers and transferred to a storage tank.

b-Weir devices

The weir type of skimmer depends on gravity to drain the oil off the surface of sea-water. The weir devices employ adjustable weirs over which the oil film, riding on the surface of the water, may flow. The recovered liquid usually collected, it may be pumped away. Once oil collected, it may be pumped into a gravity separation tank as a secondary operation. The oil separates and floats to the surface. The sea-water is discharged through valves in vessels bottom weir type skimmers generally work best with heavier, thicker oils [Schwartz, 1979, Walkup, 1971 and Sittig, 1974].

C- Centrifugal or vortex devices

Several oil recovery devices based on the use of a centrifugal force to separate oil from water. One of the interest variants of centrifugal devices is the Bertin skimmer [Pinchon, 1975].

d- The floating suction devices

The floating suction skimmer can easily be put into action by placing it on the sea-water and adjusting it to float at the oil/sea water interface. Oil accumulates at surface and sea-water is displaced through a baffled opening in the bottom. When an oil layer of sufficient depth has

accumulated it is pumped away by conventional means to storage area [Taylor, 1972 and Hopple, 1971].

1.5.2. Using of Chemicals as Oil Spill Dispersants

The use of dispersants has been, and still is, the most widely employed and immediately effective method of combating oil pollution both on open sea and on beaches. When oil, which is floating on the surface of the sea, is treated with a suitable surface-active agent and the oil is broken up into particles of different sizes. Basically, all dispersants are chemicals consisting of a polar (water –soluble group) and a non polar (oil - soluble group). Because of its amphipathic nature, the surfactant molecule locates and orients itself at the oil- water interface of an oil slick, its polar end in the water and its non-polar end in the oil. Because of this orientation it is able to reduce the interfacial tension and thereby aids in the generation of finely dispersed oil droplets. Once these oil droplets are dispersed, the surfactant will prevent them from coalescing again [Beynon, 1971].

In most cases, simply applying the surfactant to the slick is not enough [Churchill et al., 1993]. The water must also be mechanically agitated to enhance breakup of the slick into droplets. This is often done by use of a surface agitator. In recent years, however, self-mixing dispersants have been developed which form droplets on their own and do not require mixing by ships.

Dispersants have several disadvantages, the principal one being that many of them are much more toxic than the oil which they are acting on. In addition, dispersed oil may be even more toxic than non-dispersed oil because more dissolved hydrocarbons are present in the water column when the oil is dispersed. A great deal of research to

produce low toxicity oil dispersant was subsequently (after 1967) carried out and new, less toxic and more effective dispersants are developed which consists essentially of low aromatic content. At present they must be used with extreme care and only after detailed study.

The difficulty with the use of dispersants is how to apply them rapidly and effectively to the very large areas. This can be done by use of ships or aircrafts, but the application time is long, the ability to evenly distribute the dispersant is questionable, and the cost is enormous [Fingas et al., 1989]. Application of dispersants in shallow water remains an issue of debate within the spill response community. An experimental oil spill to evaluate potential environmental impacts and benefits of applying dispersants to spills in shallow water has therefore been under consideration.

Coupled three-dimensional oil spill and hydrodynamic models were used to assist in the design of such an experiment to apply oil spill dispersant. The purpose of the modeling work was to map hydrocarbon concentration contours in the water column and on the seafloor as a function of time following dispersant application. These results could assist in determining the potential environmental impact of the experiment, as well as guiding the water column sampling activities during the experiment itself. Eight potential experimental oil spill scenarios were evaluated, all of them included application of chemical dispersants to the slick shortly after release [Reed et al., 2004].

1.5.3 Using of Oil Sorbers to Control Oil Spill

The most urgent technique of elimination of oil and petroleum products is collecting of thin layers from the water surface with the help of

sorbents. Sorbents are materials that soak up liquids. They can be used to recover oil through the mechanisms of absorption, adsorption, or both, absorbents allow oil to penetrate into pore spaces in the materials they are made of while adsorbents attract oil to their surfaces but don't allow it to penetrate into the material. To be useful in combating oil spills, sorbents need to be both oleophilic and hydrophobic although they may be used as sole cleanup method in small spills. Sorbents are most often used to remove final traces of oil or in areas that cannot be reached by skimmers. Once sorbents have been used to recover oil, they must be removed from the water and properly disposed or cleaned for re-use. Any oil that is removed from sorbent materials must also be properly disposed or recycled.

Retention of oil over time, recovery of oil from sorbents, amount of oil sorbed per unit weight of sorbent, and reusability and biodegradability of sorbent are important properties of sorbent. Sorbent materials applied to oil slick changes liquid oil to a semi colloid. The oil can then be removed in an efficient and easy manner.

The characteristics of both sorbents and oil types must be considered when choosing sorbents for cleaning up spills:

- **Rate of absorption:** the rate of absorption varies with the thickness of the oil. Light oils are soaked up more quickly than heavy ones.
- **Oil retention:** the weight of recovered oil can cause a sorbent structure to sag and deform, and when it is lifted out of the water, it can release oil that is trapped in its pores.
- **Ease of application:** sorbents may be applied to spills manually or mechanically, using blowers or fans. Many natural organic sorbents that exist as loose materials, such as clay and vermiculite, are dusty, difficult to apply in windy conditions, and potentially hazardous if

inhaled.

- Good absorption selectivity of oil over water.
- Convenient shipping and storage.
- Lower density compared to water to float with or without oil absorbed.

Sorbents can be divided into three basic categories: natural organic, natural inorganic and synthetic sorbents.

Inorganic mineral products, i.e. organic synthetic products and organic vegetable products can be used as oil sorbent materials. Mineral products include perlite, vermiculite, sorbent clay, and diatomite. However, these materials do not have adequate buoyancy and their oil sorption capacity is generally low.

1.6. FUTURE TRENDS FOR OIL SORBERS

This section provides a general overview on the wide variety of sorbent materials that have been investigated for oil spill cleanup with particular emphasis on hydrophobic aerogels, zeolites, organophilic clays and natural sorbents. The review shows that various workers have successfully prepared hydrophobic silica aerogels by employing various modification procedures to incorporate chemical functionality. In this regard, a newly patented CF₃-modified silica aerogel that can be incorporated into any commercially available solid support materials like fibreglass, alumina, insulation, alumina tiles, dacron, cotton, wool, and vitreous carbon foam has, in particular have been developed for an efficient oil spill recovery. Hydrophobic zeolites and geopolymers, particularly those prepared cheaply from fly ash, aluminium refining wastes and other solid waste materials containing silica and alumina may also find an application in the removal of oil spill while

simultaneously provide a solution to other environmental problems. Organoclays have also been shown in this section to be potential candidates for use in oil spill cleanup operations, especially, granular organoclays, it was observed that, they are several times more effective than activated carbon for removal of oil from oil-water mixtures. The review have further indicated that organoclays can be used to improve the adsorption efficiency of activated carbon. Cosequently, lowering the operation costs associated with carbon even if there is no oil, or only a very small amount is present in the water. Therefore, it is suggested that mixtures of activated carbon and other porous sorbents such as hydrophobic silica aerogels, zeolites and geopolymers may be quite useful for oil sorption and recovery. Exfoliated graphite is another sorbent that has been shown to give excellent and very promising results for oil spill removal and further development of this material to increase its oil sorption capacity, oil recovery and sorbent recycling performance is therefore recommended. Synthetic sorbents such as polypropylene and polyurethane are presently the most commonly used commercial sorbents in oil spill cleanup due to their oleophilic and hydrophobic properties. It has been demonstrated too, that the oil sorption capacity of these synthetic materials can be increased by blending them with other natural products, though the blending percentage should be further optimized to obtain the best oil sorption performance. However, the non-biodegradability of these materials is a major disadvantage since landfill disposal is environmentally undesirable and incineration is very expensive. Finally, it is suggested that acetylated rice straws and other biodegradable lignocellulosic vegetable products such as cotton, wool, sugar cane, paper, wood, etc may prove very economical, technically feasible and environmentally

acceptable for application in oil spill cleanup technology.