Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties

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Abstract

This paper 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 cleanup. The discussion is especially focused on hydrophobic silica aerogels, zeolites, organoclays 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.

Keywords: porous materials, silica aerogels, zeolites, organoclays, natural sorbents, oil sorption, oil spill cleanup.

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Introduction

With another recent large spill of oil (about 12,000 tonnes) on the Spanish coast of Galicia by the *Prestige* oil-tanker, there is now a growing worldwide concern about the urgent need to control accidental and deliberate releases of oil during transportation and storage. Examples of other recent 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 and spill, the location and weather conditions [1].

A wide range of materials for oil remediation have actually been employed such as dispersants, absorbents, solidifiers, booms and skimmers [1-6]. 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 [1].

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

[4,7]. Several absorbents that exhibit at least some of these properties have been developed eg modified organophilic clays, lime, silica, exfoliated graphite, hydrocarbon and plastic polymers, cellulose-based materials and elastomers [4,7-15]. 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 [4,12,16-18]. Mineral products include materials such as zeolites, silica, perlite, graphite, vermiculites, sorbent clay and diatomite [16,18]. 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 [17,19]. A major disadvantage of these materials is that they degrade very slowly in comparison with mineral or vegetable products and are not as naturally occurring as mineral products [4,12,17,20] 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 [12,18]. Such organic vegetable products have, however, been reported to show poor buoyancy characteristics, relatively low oil sorption capacity and low hydrophobicity [12,18]. The purpose of this review is to provide a general overview of these three classes of sorbent materials that have been developed for oil spills cleanup with particular emphasis and more detailed discussion on hydrophobic silica aerogels, zeolites, organophilic clays and natural sorbents.

Mineral Products

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 for penetration of varying sizes of compounds into the solid. The combination of the sol-gel and supercritical drying techniques used for the synthesis of these materials impart into them unique properties such as large surface areas (up to 1000 m^2/g and greater), high porosity, low density and low thermal conductivity [7,10,21]. Various applications such as thermal insulation, support of catalysts, supercapacitors for electric cars, microfilters, adsorbents, controlled release of drugs,

inertial confinement fusion, etc of these materials have been investigated [10,22]. Since the first synthesis of aerogels from water glass [23], 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 [24].

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 commercialisation is the collapse of their structure due to adsorption of water. Substitution of alcohol with CO_2 supercritical drying is desirable because CO_2 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 CO_2 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, Schwerfeger et al.[25] 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 $MeSi(OMe)_3$ [25]. More recently, Yokogawa and Yokoyama [9] reported the successful preparation of very low density trimethylsilyl (TMS) modified silica aerogel that was more hydrophobic than conventional aerogels even by using the CO_2 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 [9]. 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, ^{13}C nuclear magnetic resonance (NMR) and ^{29}Si NMR to observe the existence of TMS in the aerogel [9].

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 [26]. 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. [10] 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 [10] 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. [10] 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 750-870 m^2/g for aerogel densities of 0.05-0.2 g/cm^3.

Other workers [27-30] 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 [30] and has been incorporated into silica aerogels [31] to produce a durable hydrophobic material that is useful for separation of organic materials from mixtures of organics and water. Hrubesh and co-workers [31] 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 to range from factors of ~ 30 times for low molecular weight, highly soluble solvents, to factors of 130 times for immiscible solvents [31]. Reynolds et al. [7] recently presented a report on the intrinsic oil absorbing properties of a CF_3-functionalized aerogel which was synthesised by the hydrolysis-condensation of tetramethylorthosilicate, $(CH_3O)_4Si$ and (3,3,3-trifluoropropyl)-trimethoxysilane, $CF_3(CH_2)_2Si(OCH_3)_3$, in CH_3OH by a 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 non-functionalised silica aerogel,

- has a higher oil absorbing capacity when in a non-powder 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. Table 1 shows the comparison of the CF_3-functionalised aerogel with other absorbing materials as presented by Reynolds et al. with some additions. 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 that CF_3-functionalised aerogels might perform much better than shown in Table 1 if they are used as coatings on devices.

Subsequent report by Reynolds and his co-workers [8] indicated successful synthesis of CF_3-aerogels using $(CH_3O)_4Si$ and nominally 30, 10 and 1.5 mol% of $CF_3(CH_2)_2Si(OCH_3)_3$ 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. Their results shown in Figure 1 for the 30, 10 and 1.5% CF_3-aerogels together with that for the

unmodified aerogel demonstrate clearly that the hydrophobicity of the aerogels increases with increase in the degree of modification and that the CF_3-modified aerogels are much more hydrophobic than the unmodified aerogel. The IR showed that the $CF_3(CH_2)_2$- 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 $CF_3(CH_2)_2$- 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 $CF_3(CH_2)_2$- 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 $CF_3(CH_2)_2$- group implying that they can actually absorb oil as much as 237 times their weight (Table1), much more than previously obtained [7,20]. The CF_3-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. [32] that a device formed by incorporating such hydrophobic CF_3-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.

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 [33-35]. 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 (ie they are highly organophilic). These zeolites are thermally and hydrothermally stable (up to about 1300 °C [36]) 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 [37] . 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.

• Coadsorption with water possible only when the relative humidities are higher than 70% compared with 50% for active carbon.

• Can be regenerated with steam [38,39] or by calcination at high temperatures [40,41].

One disadvantage of the hydrophobic zeolites is, however, their much less adsorption capacity for most organic components in comparison with active carbon sorbents [38].

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 [36,42]. Many dealumination processes have been developed over the years such as steaming [43,44], treatment with mineral or organic acids [45,46], or chelating agents [47], reaction with silicon tetrachloride [48,49] and treatment with silicon hexafluoride [50,51]. The surface properties of zeolites have also been modified by silylation to produce hydrophobic zeolites [52,53]. 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 [54].

Chen [55,56] was the first to propose the use of hydrophobic molecular sieves to remove organics from water. Recently, hydrophobic zeolites have also been reported [14,57] 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 [58-66]. 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 [60], thus providing a solution to other environmental problems in addition to application in the removal 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 [67].

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) [68]. 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 building waste as well from clay materials such as kaolinite and metakaolinite [68-72].

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) [73]. 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 [74] and Raussell-Colom and Serratosa [75] that many polar organics (eg 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. [76] 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 [77]. 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 [78].

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. [79], McBride et al. [80] and Evans and Pancoski [81] 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 oranophilic. 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 of 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 [82]. 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 [15]. 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 [83-85] 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 [86,87] 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 wastewater. Figure 2 shows Alther's data illustrating 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 [88-90] 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 [84,85] 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 [91] 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 [92]. 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.

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. [4] 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.

An exfoliated graphite was reported too to sorb [20,93,94] 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 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 (i) the recycling of both heavy oils and carbon materials. Their promising results on exfoliated graphite have been published in various articles [94-100]. They have also presented a review [101] 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 cabonized 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 [102] 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 on 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.

Synthetic Organic Products

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 [103]. More recently, polypropylene was observed by Teas et al. [4] 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 CF_3-functionalised silica aerogel [21,31,32], exfoliated graphite [20], actetylated rice straw [13], milkweed (Asclepias) and cotton fibers [12,104] have been developed that exhibit much higher oil sorption capacity than polypropylene fiber (or web) or polyurethane foam (Table 1). Nevertheless, it has been observed by Choi and Cloud [12] 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 [12,105], the non-biodegradability of these materials is a major disadvantage.

Natural Sorbents

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 cleanup [12,104,106-108]. 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 [12,18]. 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 [12,13,104,109]. For example, Kobayashi et al. [109] 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 [12,104] 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 [12]. These workers [12] also demonstrated that sorbed crude oil could be recovered from the natural sorbents by a simple mechanical retrieval equipment suggesting that the sorbents could be recycled several times in oil spill cleanup. Thus, the results of these workers [12] 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. [13] 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 (Table 2) and which are much higher than those obtained previously [12,104] 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 (Table 2). 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.

Conclusions

This review provides a general overview of the wide variety of sorbent materials that 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 CF$_3$-modified silica aerogel that can be incorporated into any commercially available solid support materials like fibreglass, alumina, insulation, alumina tiles, dacron and cotton wool, and vitreous carbon foam has, in particular 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 application in the removal of oil spill while simultaneously providing a solution to

other environmental problems. Organoclays have also been shown in this review to be potential candidates for use in oil spill cleanup operations, especially as granular organoclays have been observed to be several times more effective than activated carbon for removal of oil from oil-water mixtures. The review further indicates 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. It is therefore 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 clean up due to their oleophilic and hydrophobic properties. It has been demonstrated too that the oil sorption capacity of these synthetic materials can be increased further by blending them with other natural products, though the blending percentage should be further optimised 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. Lastly, it is suggested that acetylated rice straws and other biodegradable lignocelluosic 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.

Acknowledgement

Figure Captions

Figure 1. Water absorption capacity of the 30%, 10%, 1.5% and 0% (unmodified) CF_3-modified aerogels in terms of their weight gain in water-saturated air atmosphere [8].

Figure 2. Alther's data illustrating the efficiency of powdered, non-ionic organoclay for removal of various minerals from water. The efficiency of activated carbon for removal of turpentine is included for comparison [89].
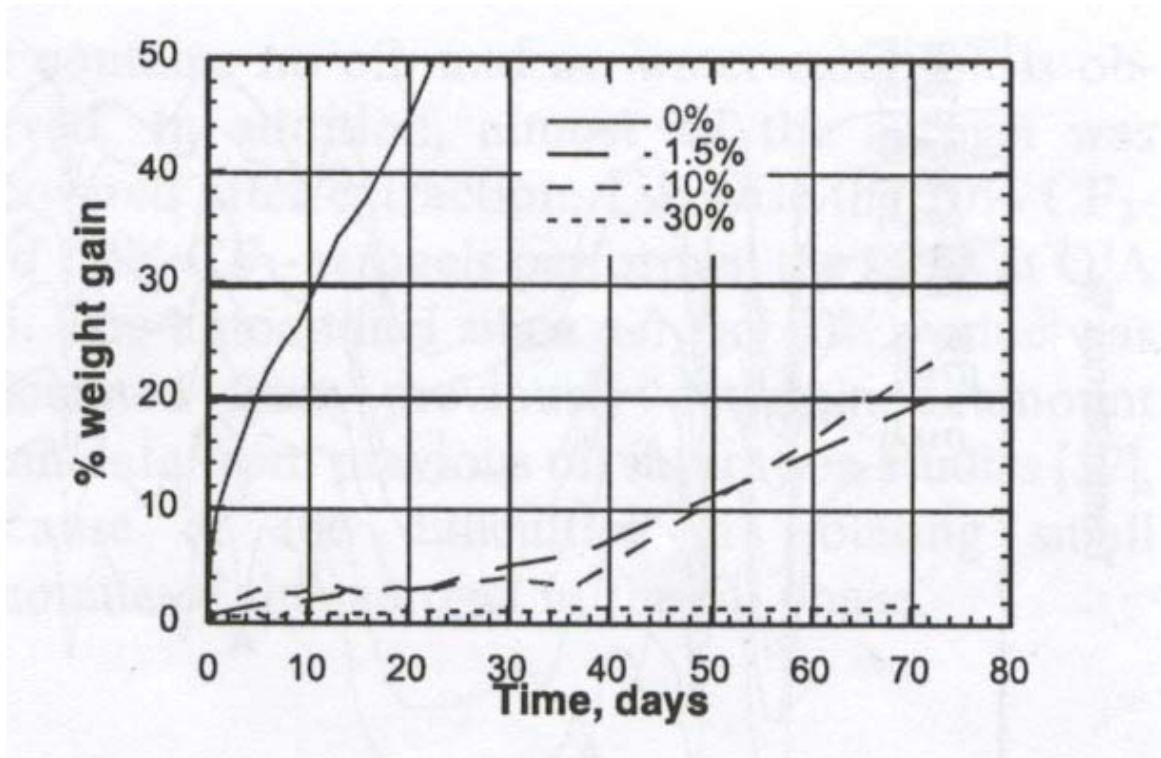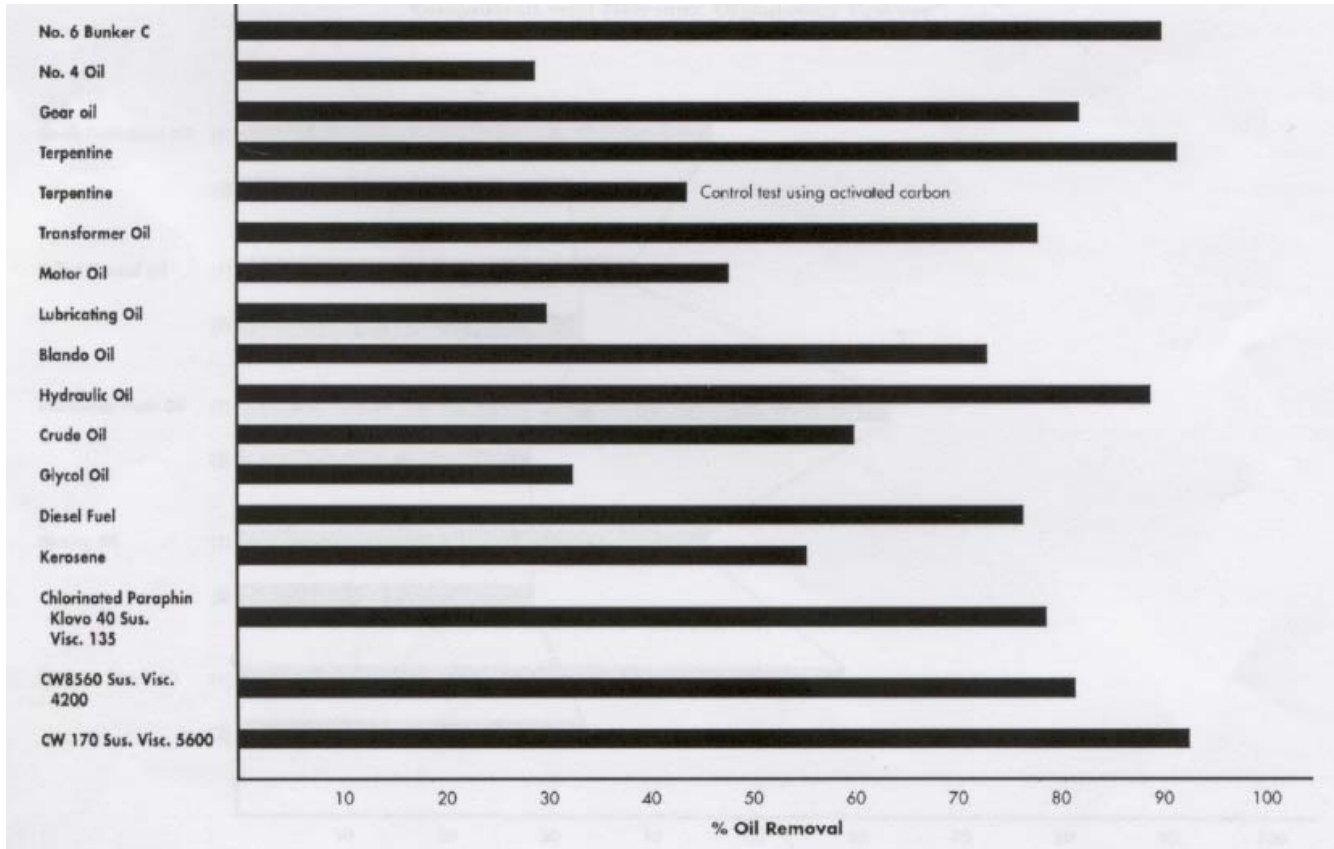
Figure 1

Figure 2

Table 1. Oil absorption capacity of selected materials [7]

Material	Oil Type	Oil Uptake[a]	Form	Ref.
Bregoil (waste-wood fibers)	crude	7 X	sponge	[110]
Urethane-isocyanate-alcohol polymer	motor	34.4	granular	[111]
Acrylate-nitrile-alcohol polymer	crude	12 X	device	[112]
Polypropylene	crude	7 X	device	[112]
Polypropylene	light crude	10 X	fibre/web	[12,104]
Polypropylene	light cycle/ heavy crude	4.5 X	non-woven web	[4]
Cellulosic fibre	light gas heavy crude	3.75 X 5 X	wooden chips	[4]
Expanded perlite	light cycle	up to 3.5 X	granular	[4]
Expanded perlite	heavy crude	up to 3.25 X	granular	[4]
Milkweed floss (*Asclepias*)	light crude	~ 40 X	granular	[12]
Exfoliated graphite	crude	80 X	device	[20]
Berthinate (hydrophobic treated peat)	crude	6 X	granular	[113]
Gum rubber + polyolefin	crude	4 X	powder	[114,115]
Clay + NR_4^+	ATF[b]	6 X	powder	[2,116]
Clay + NR_4^+	mineral	0.5 X	powder	[2,116]
Cellulose	crude	18 to 22 X	device	[117]
Polyvinylalcohol/polypropylene	motor	2 X	powder	[118]
Cellulose acetate	crude	9 X	device	[29]
CH_3SiCl_3 treated fly ash	gear	0.5 X	powder	[119]
Hydrous calcium silicate	gear	4.9 X	powder	[119]
Hydrous calcium silicate	crude	6.3 X	powder	[119]
CF_3-functionalised silica aerogel	crude	4 to 16 X	powder	[7]
CF_3-functionalised silica aerogel	crude	up to 237 X	powder	[8]
Silica aerogel	crude	< 0.1 X	powder	[7]
Acetylated rice straw	machine	16.8 to 24 X	straw	[13]

[a] Oil weight times absorbing material weight. [b] Authomatic transmission fluid.

Table 2. Yield and oil absorption capacity of acetylated rice straw obtained under various conditions in the presence of 4-Dimethylaminopyridine (DMAP) catalyst [13]

Acetylation conditions				Acetylated straw	
Solid-to-liquid ratio[a] (g/ml)	Temperature (°C)	Reaction time (h)	% catalyst by weight (% of dried straw)	Weight percent gain	Oil absorptivity (g of oil/g of straw
1:20	120	0.5	0	11.2	16.8
1:20	120	1.0	0	11.8	18.2
1:20	120	1.5	0	12.0	18.7
1:20	120	2.0	0	12.2	18.8
1:20	120	3.0	0	12.4	19.2
1:20	120	4.0	0	12.8	20.1
1:20	120	0.5	1	13.6	20.9
1:20	120	0.5	2	13.8	21.6
1:20	120	0.5	3	14.0	21.8
1:20	120	0.5	4	14.2	22.0
1:20	120	0.5	5	14.8	23.0
1:20	120	0.5	6	15.0	23.5
1:20	120	0.5	7	15.4	24.0
1:20	100	0.5	0	3.7	ND[b]
1:20	100	0.5	3	8.7	ND
1:20	100	0.5	10	9.7	ND

[a] Solid-to-liquid ratio represents ratio of dried rice straw (g) to acetic anhydride (mL).

[b] Not determined.

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