Cellulosic Substrates for Removal of Pollutants from Aqueous Systems: A Review. 3. Spilled Oil and Emulsified Organic Liquids

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Water-insoluble oils, including crude petroleum and a wide variety of refined organic liquids, can cause major problems if spilled or leaked to aqueous environments. Potential environmental damage may be reduced if the spilled oil is promptly and efficiently removed from the water. This article reviews research that sheds light on the use of cellulose-based materials as sorbents to mitigate effects of oil spills. Encouraging results for oil sorption have been reported when using naturally hydrophobic cellulosic fibers such as unprocessed cotton, kapok, or milkweed seed hair. In addition, a wide assortment of cellulosic materials have been shown to be effective sorbents for hydrocarbon oils, especially in the absence of water, and their performance under water-wet conditions can be enhanced by various pretreatments that render them more hydrophobic. More research is needed on environmentally friendly systems to handle oil-contaminated sorbents after their use; promising approaches include their re-use after regeneration, anaerobic digestion, and incineration, among others. Research is also needed to further develop combined response systems in which biosorption is used along with other spill-response measures, including skimming, demulsification, biodegradation, and the use of booms to limit the spreading of oil slicks.

Keywords: Cellulose; Biomass; Biosorption; Remediation; Pollutants; Adsorption; Petroleum; Organic solvents; Wastewater treatment; Emulsions

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INTRODUCTION

Oil, when spilled into natural waterways, oceans, or groundwater, causes harm to the environment. Natural plant and animal populations suffer both from the gross presence of the contaminant and from its possible toxicity (Annuciado 2005; Aisien 2006; Aguilera *et al.* 2010; Burton *et al.* 2010). For purposes of this review article it will be assumed that the best way to deal with such problems, short of avoiding the spills in the first place, is to swiftly and efficiently remove as much of the spilled oil as possible from the water, while minimizing any additional environmental harm resulting from the remediation.

Remediation of water-borne oily substances tends to be challenging. This is due in part to the fact that oily liquids can be present in different forms – as a separate phase, in a two-phase emulsion, or partially or totally solubilized – often simultaneously in more than one form. In addition, high expectations are often placed on the results: the remediation system should have capacity to remove large amounts of the contaminant, and it also ought to decrease the residual concentration in the water to a very low level. To make matters more challenging, oily substances in aqueous environments can be extremely diverse, and they can change substantially over time due to such processes as oxidation, degradation, emulsification, partial evaporation, *etc*. In addition, there are concerns about what can be done with a loaded sorbent material after it has been used for bioremediation; ideally one should be able to recover all the sorbed oil at high concentration by a simple, inexpensive method such as mechanical compression, making it possible to use the sorbent multiple times without loss of absorption capacity. Furthermore, the ideal sorbent material itself ought to be fully biodegradable and prepared with a minimum of adverse effects on the environment.

The present review article will explore, first of all, the hypothesis that the effectiveness of cellulose-based sorbents for the removal of petroleum and petroleum-derived fluids, organic solvents, *etc*., can be attributed to identifiable factors such as surface area, packing density, and their chemical makeup. It will then consider various available strategies that could be used to design collection processes that are optimum, environmentally friendly, and cost effective.

Definitions

The word "oil", as used in this article, implies a liquid that is substantially insoluble in water. Crude oil spills, as exemplified by the Exxon Valdez and Deepwater Horizon incidents (Aldous and Hetch 2010; Xia and Boufadel 2010; Atlas and Hazen 2011; DeLaune and Wright 2011), are clearly of major concern in terms of environmental impact. Other oils that have been unintentionally or carelessly released into waterways or groundwater include refined petroleum products, vegetable oils, silicone oils, organic solvents, and various toxic liquids. Because of their lower density, most oils of interest will float on the surface of water as thin films, as liquid "lenses", or by forming phase-separated layers. The term "oil slick" can be used to refer to a diverse class of spilled oil masses on water, recognizing that the time-dependent processes of evaporation, oxidation, and natural emulsification can greatly change properties such as reactivity and viscosity (Fazal and Milgram 1979; Bobra *et al.* 1992). It has been noted that although large single-incident catastrophes have captured most public attention, a greater net amount of release can be expected to have occurred due to such factors as perennial leakage, outfalls, and other relatively small events (Fazal and Milgram 1979; NAS 2003; Simanzhenkov and Idem 2003). Simanzhenkov and Idem (2003) estimated that the two largest sources of unintentional oil release were the operations used in petrochemical plants and the rinsing out of compartments of oil tankers.

Figure 1 presents a schematic diagram to illustrate some of the important small-scale features of a typical oil spill on water. Two types of emulsions will be considered in this review: water-in-oil (W/O) and oil-in-water (O/W). Of these, it is the formation of W/O emulsions that can dramatically change the character of a mass of spilled crude oil from a low-viscosity liquid to sticky, cohesive mixtures having a relatively high viscosity (Fingas 2011a). The ability of O/W and W/O emulsions to remain stable over time has been attributed to the presence of amphiphilic asphaltenes, a naturally occurring component of crude oils (Buckley 1998; Buckley and Wang 2002; Natarajan *et al.* 2011;

Kilpatrick 2012). The range of properties and the time-dependent nature of spilled oils pose challenges to the development of any successful program of remediation.

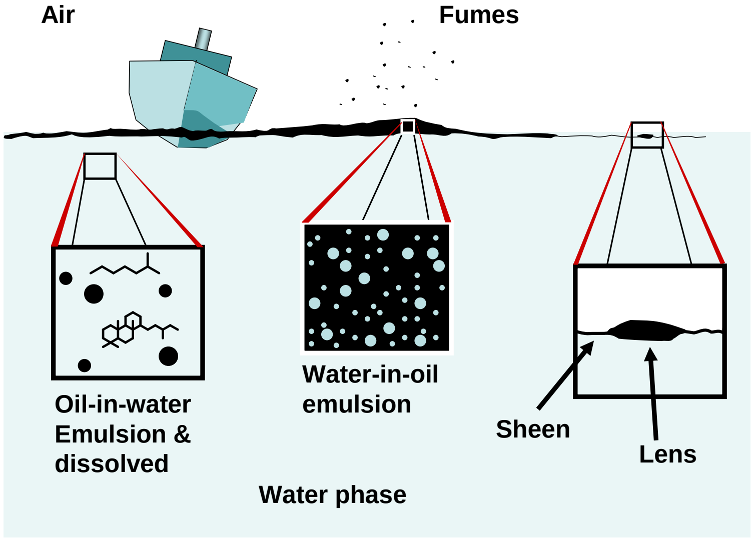

Fig. 1. Schematic diagram representing some fine-scale features of a typical oil spill on water

A further challenge with respect to complete handling of spilled oils involves the fact that finite concentrations of oil can be present in the aqueous phase in solubilized, phase-separated, or emulsified forms (Bobra 1992; NRC 2002; Ibrahim *et al.* 2009). Oil can be emulsified as droplets in water if there are sufficient surface-active species present along with agitation (Johansen *et al.* 2003). Efforts to address the environmental consequences of the soluble portion of such organic compounds go beyond the scope of the present article. Rather, Part 4 of this series of articles will deal with efforts to remediate various potentially toxic or harmful organic compounds from aqueous solutions by biosorption. Parts 1 and 2 of this series focused on biosorption of heavy metal ions and dyes, respectively (Hubbe *et al.* 2011, 2012a). The present Part 3 addresses biosorption of spilled oils and emulsified organic liquids under dry or water-wet conditions.

The Need for Improved Oil Removal Technologies

Spilled oil has both physical and toxicological effects on aquatic life (Ott 2005; Penela-Arenaz *et al.* 2009; Aguilera *et al.* 2010; Burton *et al.* 2010; DeLaune and Wright 2011). It has been shown, for instance, that if spilled oil can be quickly collected onto the surfaces of floating particles of rubber, then the survival prospects for fish in the vicinity can be substantially improved (Aisien *et al.* 2006). Time is critical due to the changing chemical and physical nature of the spilled material, and also the oil's tendency to become more spread out or dispersed with the passage of time (Perkovic and Sitkov 2008; Fingas 2011).

The effects of naturally present and intentionally added dispersants are of particular interest because they can have an adverse impact on the environment (Chapman *et al.* 2007; Berninger *et al.* 2011; CRRC 2012), and they also have the potential to make the collection of the spilled oil onto sorbent materials more difficult. On the positive side, it appears that dispersants, which are often non-ionic surfactants or their combinations with O/W emulsions (Clayton *et al.* 1993; Michel *et al.* 2005; NRC

2005), can reduce fire hazards and tar-like properties often associated with oil slicks (Atlas and Hazen 2011). Dispersants have been shown to decrease the droplet size of O/W emulsions, an effect that has been shown in the lab with certain surfactants, to accelerate natural processes of biodegradation (Varadaraj *et al.* 1995a). However, depending on the specific system and dispersant/surfactant, often no effect or a negative effect on biodegradation has been observed. Most oilfield dispersants contain an ionic surfactant that can act as a mild disinfectant. It has been reported that dispersants can increase the initial toxicity of spilled crude oil (Michel *et al.* 2005; Ott 2005; Berninger *et al.* 2011). Dispersant application near the vicinity of release at undersea drilling sites, while tending to decrease amounts of oil reaching shorelines, tends to increase the amount of emulsified oil that remains in the water column, where it adversely affects suspended (pelagic) and bottom-swelling (benthic) organisms (CRRC 2012). The presence of surfactant at a water-oil interface generally can be expected to inhibit bacteria from approaching the oil. It has been reported that dispersants can increase the probability that the material will sink to the bottom (Clayton *et al.* 1993), though this effect has been disputed (CRRC 2012). Such sinkage is considered undesirable due to the greater difficulty of collecting the oil, concerns regarding slower biodegradation, and consumption of dissolved oxygen at the ocean floor. Concentrations of oil-degrading bacteria are generally higher near the surface of the ocean and very low elsewhere. Concerns about oxygen depletion are supported by evidence of anaerobic conditions adjacent to the natural seeps of oil at the sea floor (Wardlaw *et al.* 2008).

Biosorption as a remediation strategy (review articles)

Plant-based materials have been used for many years as a tool for dealing with spilled oils (Fazal and Milgram 1979; Tookey and Abbot 1991; Choi and Cloud 1992; Choi *et al.* 1993). Some aspects of the topic of biosorption of oils have been considered in earlier reviews (Adebajo *et al.* 2003; Aksu 2005; Bayat *et al.* 2005; Fingas 2011a). Also, it needs to be recognized that cellulosic materials constitute just one of several promising classes of sorbents that have been evaluated relative to their ability to absorb spilled oil. Other substrates that have been considered include polypropylene (PP) fibers (Zahid *et al.* 1972; Phifer and Costello 1992; Wei *et al.* 2003), exfoliated graphite (Inagaki *et al.* 2000a), coal (Rethmeier and Jonas 2003), wool (Radetic *et* al 2003; Rajaković-Ognjanović *et al.* 2008), chitosan (Ahmad *et al.* 2005a,b), specialty polymers with oil-compatible groups (Jin *et al.* 2012), highly hydrophobic sponges (Reynold *et al.* 2001; Gui *et al.* 2010; Choi *et al.* 2011; Moura and Lago 2011; Zhu *et al.* 2011a), and inorganic materials such as perlite, vermiculite, and bentonite (Teas *et al.* 2001; Ahmad *et al.* 2005b; Curbelo *et al.* 2006; Moura and Lago 2011).

Cellulosics can sorb as much or more oil as some polypropylene materials

While various synthetic polymer sorbents have been shown to be very effective for sorbing oil (Zahid *et al.* 1972; Phifer and Costello 1992; Wei *et al.* 2003), quite impressive results already have been achieved with the use of natural plant materials. Fibers obtained from kapok and milkweed have been found to have a similar or even a greater capacity to sorb oil from the water surface in comparison with typical polypropylene (PP) products that have been more often employed for this purpose (Knudsen 1990; Choi and Cloud 1992; Choi *et al.* 1994; Choi 1996; Hori *et al.* 2000; Deschamps *et al.* 2003a; Khan *et al.* 2004; Huang and Lim 2006; Lim and Huang 2007a). Unprocessed cotton and ordinary papermaking fibers, as well, have shown an ability to take up oil – even when wet – at capacity levels similar to that reported for PP (Johnson *et al.* 1973; Deschamps *et al.* 2003a; Payne *et al.* 2012).

An advantage of using natural products is their biodegradability. If loose PP fibers fail to be collected after their deployment, then they can be expected to persist in the environment (Longo *et al.* 2011). By contrast, cellulosic fibers can be expected to biodegrade if not collected, for instance if they happen to break free from an absorbent boom, *etc.*

Currently Used Technologies for Dealing with Oil Spills

Systems aiming to minimize the environmental impact of oil spills ideally should fit into an integrated response strategy employing a variety of effective measures that are in current use. State-of-the-art oil spill response strategies have been reviewed (Cumo *et al.* 2007; Perkovic and Sitkov 2008; Vanem *et al.* 2008; Graham 2010; Dave and Ghaly 2011; Fingas 2011a; 2012; ITOPF 2012). Table 1 lists some of the most commonly applied measures taken in response to off-shore oil spills. Some additional discussion follows, related to items in the table.

Table 1. Common Measures Taken in Response to a Maritime Oil Spill

Action Taken	Main Purpose of Action	Limitations	Selected Literature Citations
Containment boom use	To impede spreading of an oil slick	Limited to low sea states and currents	NOAA 2010a
Skimming of oil from water surface	To scoop up floating oil at water surface	Limited to low sea states and currents	Fingas 2011a
Gravity or centrifugal separation	To separate oil after skimming	Limited to untreated medium-weight oils	Sharma 2011
Burning of oil at water surface	To convert floating oil into gases & residue	Pollutes the air; works best for thick layers	Evans *et al.* 2001; Fingas 2011b
Dispersant application to oil slick	To break up and disperse oil slicks into small O/W droplets	Increases toxicity & may resurface	Michel *et al*. 2005 NRC, 2005
Other treating agents – *e.g.* solidifiers	To enable oil recovery as a solid	Decreases potential to recover liquid oil	Rosales *et al*. 2010
Absorbent use as loose material	To remove oil from the liquid phase	Needs to be collected after being spread	Choi and Cloud 1992
Absorbent use as assembly	To remove oil from the liquid phase	Needs to be collected after being placed	Fingas 2012a
Biodegradation	To remove toxicity of sediment or sorbent	Takes a very long time in nature	Correa *et al.* 1997
Berms built to block shore	To keep oil slick away from marshland, *etc*.	Causes damage to the shoreline	Aldhous & Hetch 2010; Natl. Commission 2011
Scouring or removal of sediments	To remove oil from the shore or bottom	Sterilizes sediment, slowing recovery	NOAA 2010b

Use of containment booms

Floating booms can be used as a strategy to prevent oil from spreading out over a wider area (ITOPF 2012 NOAA 2010a; Fingas 2011a). The effectiveness of booms depends not only on the design of the boom itself, but also on the currents and wave height. Booms are strongly limited by the fact that currents over 0.8 knots (0.4 m/s) will carry oil underneath. Further, waves over about 1 m and winds more than about 10 knots (5.1 m/s) can be expected to allow oil to pass either over the top or underneath the barrier.

Skimming of floating oil

Because most petroleum products, including most crude oils, are light enough to float on water, oil often can be effectively "skimmed" from the water surface by use of specialized equipment (Fingas 2011a). The use of booms and skimmers remains the primary oil spill recovery method at this time. Relatively calm weather conditions are required, however, for such equipment to be effective, and there needs to be a reasonable thickness of floating oil, *e.g.* a few mm or more. The current limitations for skimming are similar to those required for booms (< 0.8 knots or 0.5 m/s – relative to current). Similarly, the wind and wave limitations are the same as they are for booms (1 m waves and 10 knots (5.1 m/s) wind). Containment booms can be used to hold the floating oil in place long enough to allow the effective use of a skimmer. Table 2 summarizes a variety of skimmer types and their (water) recovery potential (Fingas 2012a).

Table 2. Performance of Some Skimmers

Skimmer Type	**Recovery Rate (m^3/h) ***			**Percent Oil****
	Light Crude	**Heavy Crude**	**Heavy Fuel**	
Oleophilic Skimmers				
disc	0.2 to 2	0.2 to 10		80 to 95
brush drum	0.5 to 20	0.5 to 2	0.5 to 2	80 to 95
brush belt	15 to 30	1 to 10	1 to 10	80 to 95
drum	0.5 to 30			80 to 95
belt	1 to 20	3 to 20	3 to 10	75 to 95
rope mop	2 to 20	2 to 10		80 to 95
Weir Skimmers				
small weir	0.5 to 5	2 to 20		20 to 80
large weir	30 to 100	5 to 10	3 to 5	50 to 90
Elevating Skimmers				
paddle conveyer	1 to 10	1 to 20	1 to 5	10 to 40
Submersion Skimmers				
large	1 to 80	1 to 20		70 to 95
Suction Skimmers				
small	0.3 to 2			3 to 10
large trawl unit	2 to 40			20 to 90
large vacuum unit	3 to 20	3 to 10		10 to 80

* Recovery rate depends on the thickness of the oil, type of oil and sea state

** Percentage of oil in the recovered product.

Because one can expect the skimming process to collect a mixture of oil and water, some form of separator device or flotation tank or pool may also be needed (Fingas 2012a). Decanting the water directly from a recovery tank is now an option in some countries (Fingas 2012a). Enhanced gravity separation is frequently used at some spill sites (Hellmich 2011). Centrifugation is also used, since such technology can greatly speed up the separation of phases that differ in density (Sharma 2011). If the water and oil phases have been subject to emulsification, then the separation of the phases can be more challenging (Zouboulis and Avranas 2000).

Membrane use to separate oil from water

A variety of approaches based on membrane filtration have been considered as a possible alternative or substitute for density-based separation, especially when the oil is present as an emulsion. Studies have shown that O/W emulsions can be separated into their respective oil and aqueous phases by use of a suitable membrane or packed bed (Zaidi *et al.* 1992; Lee and Han 1993; Juang and Jiang 1994; Hlavacek 1995; Koltuneiwicz and Field 1996; Matsumoto *et al.* 1999; Sun *et al.* 1998, 1999; Tirmizi *et al.* 1996; Briscoe *et al.* 2000; Hong *et al.* 2002; Kocherginsky *et al.* 2003; Zou *et al.* 2003; Li *et al.* 2009). While most attention has been focused on uses of hydrophilic membrane materials, the feasibility of using hydrophobic membranes also has been demonstrated (Daiminger *et al.* 1995).

Burning of floating oil in place (toxic emissions possible)

Sometimes a floating oil slick has been set afire (Fingas 2011b). *In-situ* burning is recognized as a viable alternative for cleaning up oil spills on land and water. When performed under the right conditions, *in-situ* burning can rapidly reduce the volume of spilled oil and eliminate the need to collect, store, transport, and dispose of recovered pollutant. *In-situ* burning can shorten the response time to an oil spill, thus reducing the chances that the oil will spread on the water surface and thereby aiding in environmental protection.

What remains after an *in-situ* burn are mainly carbon dioxide, water, some smoke particulates, and unburned oil (residue). Sufficient information is now available to predict levels of these emissions and calculate safe distances downwind of the fire (Fingas 2011b). *In-situ* burning was used extensively at the DeepWater Horizon spill, where it achieved high removal rates (Aurell and Gullett 2010). Measurements at these burns showed that the levels of emissions were acceptable, especially since the burning was carried out far from the shore.

The combustion products are of concern. These include the smoke plume, particulate matter precipitating from the smoke plume, combustion gases, unburned hydrocarbons, organic compounds produced during the burning process, and the residue left at the burning pool site. Soot particles, although consisting largely of carbon, contain a variety of absorbed and adsorbed chemicals (Fingas 2011b)

Dispersing oil as an O/W emulsion

As noted earlier, dispersants are sometimes employed as part of a response program to deal with an oil spill (Atlas and Hazen 2011). A study by Varadaraj *et al.* (1995a) showed that addition of a surface-active agent to an agitated crude-oil-water system yielded a smaller droplet size. The same study showed that, although some dispersants have been reported to delay biodegradation, a blend of ethoxylated and non-ethoxylated sorbitan oleates had an accelerating effect on biodegradation, even beyond what would have been expected due to the increased surface area of the more finely dispersed O/W emulsion.

A key question to consider is whether such treatments may render the oil less amenable to subsequent collection by sorbents. In principle, the use of a dispersant will increase the colloidal stability of an oil droplet suspended in water (Adamson and Gast 1997). One would expect that a more stable droplet would be less likely to be collected onto a solid surface; however, there is a need for further study to test the validity of this assertion in the case of typical crude oils, dispersants, and sorbent materials.

Treating the oil with other agents such as solidifiers

Soldifiers are intended to change liquid oil to a solid compound that can be collected from the water surface with nets or mechanical means (Fuller 1971; Rosales *et al.* 2010; Fingas 2011a; Fingas and Fieldhouse 2011). They are sometimes referred to as gelling agents or collecting agents. Collecting agents are actually a different category of materials that are the opposite of dispersants and are not yet fully developed. Solidifiers consist of either cross-linking chemicals, that cause two or more molecules to couple together, or polymerization catalysts, that cause molecules to link to each other. Solidifiers usually consist of powders that rapidly react with the oil.

Depending on the agent, about 10 to 40% by weight of the solidifying material is required to change the behavior of the oil, under ideal mixing conditions. Solidifiers have not been used in the past for a number of reasons. Most importantly, if oil is solidified at sea, it makes recovery more difficult, as skimming equipment, pumps, tanks, and separators are built to deal with ordinary liquids or very viscous liquids. Secondly, the amount of agent required to solidify oil is generally so large that it would be impractical to treat even a moderate sized spill.

Absorption of the oil (liquid absorbed by solid particles)

Oil remediation strategies involving absorption onto solids can be viewed, once again, as a way to change the phase of the spilled material (Browers 1982; Pate 1992). Rather than dealing with a liquid material, the oil is incorporated into something solid. The ideal would be to have this transformation occur relatively soon after a spill event, before the oil has had sufficient time to spread and increase in viscosity (Fingas 2011a). Later sections of this article will focus on various aspects of absorbent use. Sorbents are well suited for collection of the remnants of floating oil – either as a “sheen” of oil or as floating droplets – after other measures have been taken. For instance, though direct physical collection of oil with a skimmer makes sense for relatively thick layers of oil, such operations are not expected to be effective for handling relatively thin layers of oil, such as sheens (Fingas 2011a). When left uncontained, floating oil can spread and cover a very large area. Simanzhenkov and Idem (2003) estimated that 1 kg of light oil will typically spread to cover up to 12,000 m^2 of water surface.

Building of berms

As an oil slick approaches a shoreline, having passed the point where it could feasibly have been contained by booms, a possible last line of defense can involve piling up soil into a makeshift dam, *i.e.* a berm (Aldhous and Hetch 2010; National Commission 2011). There are two problems. First, a berm is at best a temporary solution. Oil will likely be forced over such a berm when the next major storm occurs. Second, the excavation or dumping of material to erect the booms constitutes an immediate, clearly visible disruption of the shoreline. Such blocking off of the sea access of an estuarine marsh area with a berm disrupts the natural tidal environment.

Removal and cleaning of sediments

Some of the most unsightly damage from oil spills occurs when the oil washes ashore, and one possible response is to remove or wash oil-contaminated soil or sand (Aldhous and Hetch 2010). Simanzhenkov and Idem (2003) describe how a pump can be used first to pull as much oil as possible out of soil, after which the soil can be collected and "burned" to decontaminate it before it is returned to its original place. Questions have been raised as to whether such treatments might do more harm than good, since the vegetation surviving the initial exposure to oil might be killed by the washing or removal of the sediment (Aldhous and Hetch 2010). Likewise, it has been reported that detergent and related washing treatments can harm micro-organisms that might otherwise have assisted in decomposition of the spilled oil (NOAA 2010b).

As indicated by the last two items at the bottom of Table 1, there are no highly favorable solutions available once a layer of oil has covered sediments, especially in marshy areas of estuaries. As shown in the table, the overall response strategy may be partly dictated by the weather and by the availability of equipment such as containment booms, skimmers, and separation equipment.

The Need for a Fully Renewable Approach

Table 3 presents a brief summary of some potential environmentally responsible ways to handle oil-loaded sorbent material after its use. These and other potential strategies will be discussed at greater depth near the end of this article.

Table 3. Alternative Approaches to Minimize the Environmental Impact of Oil-loaded Sorbent Material

Strategy	Indications	Limitations	Literature Citations
Regeneration and re-use	Oil sometimes can be released by squeezing.	Single use may be cheaper & easier.	Choi *et al.* 1993; Silva-Tilak 2002
Removal of water and incineration	Use heat value from oil & biomass.	Dewatering can be slow or expensive, and legislation may prohibit incineration.	Chouchene *et al.* 2012; Vanem *et al.* 2008
Composting with oil-degrading bacteria	Accelerate biodegradation under controlled conditions.	Extensive research is needed; process may be slow.	Ghaly & Pyke 2001; Suni *et al.* 2006; Kristanti *et al.* 2011
Anaerobic digestion with bacteria from natural oil seeps	Accelerate biodegradation under controlled conditions.	Extensive research is needed; process may be slow.	Alimahmoodi & M. 2011; Ji *et al.* 2011; Mohan *et al.* 2011

Assuming that a combination of the strategies listed in Table 3 can be used to effectively and responsibly deal with an oil-loaded biosorbent, it will be important to consider factors that tend to make one sorbent material more or less promising than others. The next section will consider factors affecting the sorption capacity.

FACTORS AFFECTING OIL UPTAKE BY CELLULOSIC SORBENTS

The capacity of cellulose-based (or other) sorbent materials to take up oily liquids depends on many factors. Factors related to the sorbent material will be considered first, followed by factors pertaining to the oil, and then factors related to the aqueous environment in which oil may be present. A compilation of published data on the factors affecting oil uptake by cellulosic sorbents is described first.

Tabulation of Published Data

As shown by the headings in Table A (see Appendix), items from the literature are tabulated with references to the properties of the oil, the properties of the sorbent, the reported absorption capacity, whether or not the regeneration of the sorbent was demonstrated, the percentage loss of capacity upon repeated use of the sorbent, and various other notable findings. The literature citation is given in the last column. A key to various codes used is given below the table. The first column of Table A indicates whether the oil in the respective study was not emulsified (Not), or present as an oil-in-water emulsion (O/W). Surprisingly, none of the surveyed studies considered the collection by sorbent materials of oil from a water-in-oil (W/O) emulsion. As shown in the "oil type" column, a very wide range of oils have been considered, and the same was true in the case of "Sorbent type". The column headed "Dry? Wet?" pertains to the condition of the sorbent at the time that it was exposed to the oil. The code letter "L" means that the investigators placed a *layer* of oil on top of a pool of water, thus roughly simulating the spillage of oil onto water. The codes "D" and "W" just mean dry and wet, respectively. Under "Modification", the code "-" means that the sorbent material was not modified. The column "Assembly" indicates whether the sorbent was in the form of loose fibers (L), a packed bed (PB), non-woven (NW) fabric, needlepunched (NP) fabric, foam material (F), or as a pad of unspecified construction (P).

Properties of the Substrate

Given the wide range of available cellulosic materials, multiplied by numerous types and levels of their possible physical and chemical treatments, criteria must be developed for selecting promising sorbents for spilled oil. Though many aspects of this selection – such as the floatability of the material – need to be considered, the first point of focus in the subsections that follow will be on capacity, *i.e.* how much oil is collected by a unit mass of sorbent.

Type of substrate

As shown in Table 4, the median value for oil sorption capacity (expressed as mass of oil per mass of dry sorbent material) based on all of the studies considered (see Table A), was 10 g/g. The lowest sorption capacity (a negligible value) was reported for palm empty fruit bunch fibers (Rattanawong *et al.* 2007). The highest listed value of sorption capacity (102 g/g) corresponds to beads prepared from a specialty copolymer with cyclodextrin, a product carefully formulated for such high performance (He *et al.* 2012). Higher sorption capacities have been observed only in systems incorporating inorganic components (not listed in Table 4), such as fluorinated silica aerogels (237 g/g) (Reynolds *et al.* 2001).

Table 4. Summary of Oil Sorption Capacity Data from Table A (g oil/g sorbent) *

Sorbent Type	All Data Combined	Kapok, Milkweed, & Cotton	Hydrophobized Biomass	Other Biomass	Synthetic Fibers
Median	10	30	12	5	14
Mean	17	28	18	10	23
Minimum	0	1	1	0	0.2
Maximum	102	62	47	90	102
Count	340	47	24	150	70

* Calculations to obtain the values in this table considered the lowest and highest values for each condition from each study listed in Table A. Only data for organic sorbents (biomass-derived or petroleum-derived) are included.

Because the categories shown in Table 4 comprise very wide ranges of oil types, conditions of sample preparation, conditions of exposure, and other factors such as aqueous composition, it is reasonable to expect a broad distribution of capacity values within the data. However, by comparing median or mean values, as shown in Table 4, some general trends can be developed. It is notable, first of all, that the category of “Kapok, milkweed, and (unprocessed) cotton” showed the highest median sorption capacity. Intermediate sorption capacity was shown by synthetic sorbent materials, which included a wide assortment of products. This was followed closely by cellulosic fiber products that had been rendered hydrophobic by chemical treatment. The remaining biomass products (not including kapok, milkweed seed hairs, unprocessed cotton, or hydrophobized fibers) generally showed lower sorption capacities. Based on the previous observations, it makes sense that beyond the type of sorbent, it is most relevant to consider in detail the physical characteristics that affect the sorption capacity, including the size (surface area), moisture, density, and chemical composition. Such items are introduced next.

Particle size and surface area

If one assumes a model in which oil sorbs mainly onto the outside surfaces of the sorbent material, then it would be expected that the increased available surface area from smaller particles of sorbent would lead to higher levels of sorption capacity per unit mass. Indeed, such a relationship has been demonstrated in some cases involving loose sorbent media (Aisien *et al.* 2006; Lee *et al.* 2007; Varghese and Cleveland 2008). For example, Aisien *et al.* (2006) ground up used automobile tires and used screens to prepare subsamples with different ranges of particle size. The highest capacity to collect crude oil was observed when using the finest fraction of the ground rubber particles. Likewise, when using fibrous biosorbents, Johnson *et al.* (1973), Phifer and Costello (1992), Wei *et al.* (2003), and Husseien *et al.* (2009a,b) observed the highest sorption capacity for oil when using the finest denier fibers. An exception to the rule, regarding the size of sorbent particles, has been observed for a highly viscous oil; in such a case coarse particles can be an advantage (Ribeiro *et al.* 2000). Likewise in the case of fibrous sorbents, sometimes the larger pores between relatively coarse fibers can be advantageous for rapid take-up of crude oil (Browers 1982).

Surprisingly, only a few researchers have correlated oil sorption capacity to the measured surface area of the sorbent material (Miyata 1999; Ludwick *et al.* 2003). This is in contrast to the great many studies showing strong correlations between sorbent surface area and the capacities to sorb either heavy metals or dyes from aqueous solution (see Parts 1 and 2 of this series, Hubbe *et al.* 2011, 2012a). Whereas the heavy metal ions and dyes under consideration mainly are present in solution, the present article is concerned with either layers or droplets of oil, *i.e.* different phases.

Effects of drying

Caution is required when interpreting data related to the surface area of cellulosic sorbents, since the reported surface areas depend not only on the method employed for the determination, but also on the procedures by which the sorbent material was prepared for the surface area determination. The Brunauer-Emmett-Teller (Brunauer *et al.* 1938) method for determining surface area, usually based on adsorption of nitrogen gas, requires complete drying of the sample before the analysis. Past research has shown that the pore structure of certain cellulosic materials can be profoundly changed during the course of ordinary drying procedures. For instance, the mesopore structures within kraft pulp fibers have been shown to close up almost completely upon drying in air, with only partial reversibility upon rewetting (Stone and Scallan 1966). Such effects have been confirmed by tests with dye adsorption (Gruber *et al.* 1996). Consistent with this, the sorption capacity of plant tissue has been shown to decrease markedly when it is dried (Choi and Huber 2009).

In order to avoid unintended changes in the pore structure of sorbent material, and still be able to employ the BET analysis to represent what the surface area would have been in the wet state, it is necessary to dry the material in a special way. For instance, Stone and Scallan (1966) exchanged the water solution with organic solvents having low surface tension, then used freeze-drying to avoid closure of the pore structure during drying.

Bulk density and available pore volume

Another hypothesis to consider is that the amount of oil taken up by a cellulosic sorbent ought to be related to the available void volume within a structure. In a packed bed arrangement this would imply a relationship between oil sorption and packing density or “bulking tendency” of the sorbent. Indeed, many studies have shown higher sorption capacities for oils in the case of sorbent materials that resisted tight packing (Browers 1982; Choi *et al.* 1994; Inagaki *et al.* 2002a,b; Abdullah *et al.* 2010). Bulky fibers or bulky nonwoven material composed of such fibers also have shown particular promise for oil sorption (Knudsen 1990; Pate 1992; Pasila 2004; Korhonen *et al.* 2011). Zahid *et al.* (1972) found that there was an optimal spacing between fibers in a mat for absorbing oil. Gupta (1988) presented a model that predicted pore size and pore volume in fibrous structures as a function of construction parameters. The investigation showed that increasing the denier (cross-sectional size) of fibers in a given material, or for the same denier, choosing fibers that were of lower density, led to pores of larger size. Larger pore volume and pore size favored higher sorption capacity and higher rate of fluid take up. Needled nonwovens that provided channeled structures, which resisted collapse or significant change during sorption and handling, gave most promising results in investigations involving cellulosic and synthetic fibers (Gupta and Hong 1995). Accordingly, a highly bulky structure with large pores appears to be well suited for sorbing viscous oils (Choi *et al.* 1994). By contrast, factors such as crosslinking that reduce or constrain the bulk of sorbent materials such that they cannot swell have been shown to reduce oil uptake (Choi 1996; Gupta *et al.* 1995; Sreekala *et al.* 2008).

Floating ability

Closely related to density and pore volume is the ability of a sorbent material to float on water, which has been listed as a desirable or even an essential property for oil cleanup by many authors (Fuller 1971; Pushkarev *et al.* 1980; Ericsson *et al.* 1985; Pate 1992; Deschamps *et al.* 2003a; Wang *et al.* 2010; Korhonen *et al.* 2011; Likon *et al.* 2011; Moura and Lago 2011). Presumably, if a sorbent material cannot float on water, then there is a likelihood that it will sink, together with any sorbed oil. Once it reaches the bottom of the body of water, it can be environmentally harmful (Fingas 2011a). Even if the sorbent material is able to float initially, usually due to air entrapped between its component fibers or particles, it may gradually sink as water or oil forces its way into the material as a consequence of waves and time (Brower 1973; Lee *et al.* 2007).

Springback

The ability of a sorbent material to recover its void volume after having been compressed, *i.e.* its “springback”, can be important for certain processing strategies to be discussed. Springback depends on the elastic nature of the material. Typical cellulosic materials exhibit substantial elastic recovery after the compressive forces have been released (Wolcott and Shutler 2003). In particular, one of the outstanding features of ground rubber tire material is its strong springback ability when incorporated into a sorbent material used for oil collection (Lin *et al.* 2010). Various high-performing oil-sorbing materials, such as superhydrophobic sorbents, have been designed to take advantage of high elastic recovery after squeezing (Pushkarev *et al.* 1980; Rao *et al.* 2007; Choi *et al.* 2011).

Lumen of the fiber

Several groups of researchers have suggested that wicking of oil into the lumens of cellulosic fibers can account for a significant proportion of the observed sorption (Choi *et al.* 1993, 1994; Knudsen 1990; Lee *et al.* 2007; Lim and Huang 2007a; Abdullah *et al.* 2010; Dubey *et al.* 2012). A later section will consider ways in which the wettability of sorbent surfaces by oil and by water can influence the take-up of fluids, including that imbibed in the pores.

Holdup strength or resistance to unintended release

A number of authors have stressed the importance of employing types of sorbent materials that hold oil firmly, resisting its release after absorption (Browers 1982; Nenkova 2007; Ibrahim *et al.* 2009). It is not usually clear how such an ability might be related to the physical structure and/or the chemical composition of a sorbent. The presence of lumen structure, as mentioned earlier, has been considered as a contributing factor in the secure holding of oil after its collection (Abdullah *et al.* 2010). The mesoporous structure of a cellulosic fiber, depending on its water-swollen nature (Stone and Scallan 1966; Hubbe *et al.* 2007), also can be expected to imbibe and hold the fluid. In other words, the oil may partly or fully replace air or water already present in the pores, within which fluids are held by capillary forces (Washburn 1921; Choi *et al.* 1993; Adamson and Gast 1997; Ribeiro *et al.* 2000; Inagaki *et al.* 2002b). Some studies, however, have reported substantial leaching of absorbed oil from synthetic fiber sorbents after the collection (Wei *et al.* 2003; Khan *et al.* 2004). Many factors can influence such release, including changes in the chemical properties of the fluid or in the chemical and physical properties or structure of the sorbent. More specifically, biodegradation of the two materials (sorbed and the sorbent), relaxation of stresses in the fibers of the sorbent, and any shift in the structure may be a suitable explanation for the release of absorbed oil. Further research is needed in this area to understand more fully the absorption and desorption of oil by sorbents and to develop criteria for optimally selecting and utilizing materials. This will be particularly important for materials of natural origin, since the mesoporous nature of water-swollen cellulosic fibers may offer advantages in resisting the release of collected oils.

Water uptake and the critical surface tension of the sorbent surface

The critical surface tension γ_c of a solid, as introduced by Zisman (1972), can be defined as the highest surface tension of a series of probe liquids that will completely wet the surface. Strong correlations have been found between values of γ_c and sorption characteristics (Piao *et al.* 2010). In particular, lower values of γ_c have been associated with a lower tendency to absorb water (Tavisto *et al.* 2003; Baltazar-y-Jimenez and Bismarck 2007). Many authors have listed a low tendency to absorb water as a desirable or even essential attribute of oil-spill-control sorbent materials (Pate 1992; Choi 1996; Sun *et al.* 2002, 2003; Rethmeier and Jonas 2003; Wei *et al.* 2003; Suni *et al.* 2004; Wang *et al.* 2010; Choi *et al.* 2011). Also, in some cases, a correlation has been noted between fibers' tendency to exclude water and their tendency to float on water (Ericsson *et al.* 1985; Rethmeier and Jonas 2003; Wang *et al.* 2010; Korhonen *et al.* 2011; Likon *et al.* 2011). Reduced amounts of water sorption have been reported for a variety of sorbent materials following treatments intended to reduce the γ_c value (Sun *et al.* 2002, 2003; Choi *et al.* 2011). As a possible alternative to hydrophobizing the bulk of the absorbent itself, DePetris (1993) patented a system in which low-cost sorbent materials were encased in a hydrophobic, water-impermeable but oil-permeable, fabric layer. Wood fibers were claimed as one of the likely types of fillers to be used in such a system.

A very low value of γ_c, especially if it is lower than that required to exclude water, generally offers no further benefit in terms of oil uptake. In fact, some reports have shown less uptake of oil onto dry hydrophobized fibers in comparison to their untreated counterparts (Hubbe *et al.* 2012; Payne *et al.* 2012). Possible reasons will be considered later.

Chemical composition of the substrate surface

Differences in chemical composition of sorbent materials have been mentioned by various authors to account for differences in oil sorption capacities (Ribeiro *et al.* 2000; Choi and Huber 2009). In particular, many reports have attributed the hydrophobic nature of kapok fiber, milkweed down, and unprocessed cotton to the presence of natural waxes on their surfaces (Johnson *et al.* 1973; Pate 1992; Choi and Cloud 1992; Choi *et al*. 1994; Choi 1996; Hori *et al.* 2000; Ribiero *et al.* 2000; Deschamps *et al.* 2003a; Carmody *et al.* 2007; Lee *et al.* 2007; Lim and Huang 2007a; Abdullah *et al.* 2010). Such assertions are supported by a study in which extraction to remove natural waxy coatings rendered the fibers more hydrophilic and less capable of excluding water (Lim and Huang 2007b). Witka-Jezewska *et al.* (2003) showed that a waxy layer on barley straw contributed to a somewhat hydrophobic character when initially exposed to water. The straw became more wettable (lower contact angle) by both water and by oil following extended exposure to water; however, oil spread readily on the material regardless of such changes. Carmody *et al.* 2008 detected an increased heat of evaporation of oil that had been adsorbed onto untreated cotton, and effects that were attributed to its waxy surface.

Chemical modifications to render cellulosic sorbents more hydrophobic

The importance of chemical composition at the sorbent surface has been demonstrated most clearly by studies in which the substrate was chemically derivatized. Increased uptake of oil onto cellulosic substrates has been shown following alkylation, which made the materials more hydrophobic (Ball 1973; Maurin *et al.* 1999; Sun *et al.* 2002, 2003; Ludwick *et al.* 2003; Deschamps *et al.* 2003a,b; Adebajo and Frost 2004; Dankovich and Hsieh 2007; Rattanawong *et al.* 2007; Said *et al.* 2009; Sathasivam and Haris 2010; Bayer *et al.* 2011; Tao *et al.* 2011; Gao *et al.* 2010, 2011, 2012; Cervin *et al.* 2012; Payne *et al.* 2012). Alternatively, wax can be applied to render the surfaces more hydrophobic and more capable of sorbing oil (Raible 1990). One of the most basic and practical ways to change the surface chemical nature of cellulosic materials is by drying them or by applying heat to dry fibers; such measures have been shown to make woody biomaterials more hydrophobic (Saiton *et al.* 1996; Yamamoto 1998). Presumably, heating in air allows oleophilic components to migrate to the surface (Swanson and Cordingly 1959). Kumagai *et al.* (2008) showed that carbonizing various cellulosic materials first at 300 ^{o}C, then with further treatment at 500 ^{o}C, yielded modest increases in the absorbed amounts of various low-viscosity oils.

Acetylation has been widely studied as a means of rendering cellulosic materials less hydrophilic and more suitable for sorbing oil (Sun *et al.* 2002, 2003; Adebajo and Frost 2004; Adebajo *et al.* 2003). Even greater benefits, in terms of oil sorption capacity, have been demonstrated when cellulosic structures have been derivatized with longer-chain alkyl groups (Ball 1973; Maurin *et al.* 1999; Deschamps *et al.* 2003a,b; Ludwick *et al.* 2003; Dankovich and Hsieh 2007; Said *et al.* 2009; Cervin *et al.* 2012) or with oil-loving cyclodextrins (Ding *et al.* 2011; He *et al.* 2012). Rosin, a hydrophobic agent that is often used to reduce the water-absorptivity of paper, has been shown also to improve the ability of papermaking fibers to take up oil (Ericsson 1985). Likewise, the alkaline sizing agent alkenylsuccinic anhydride (ASA) has been shown to enhance oil uptake under water-wet conditions (Payne *et al.* 2012). Recently there also has been interest in the deposition of hydrophobic nanoparticles to render a surface highly hydrophobic (Stanssens *et al.* 2011).

Properties of the Oil

The term “oil” covers a wide variety of compositions and respective physic-chemical behaviors. In brief terms, oil can be defined as a water-insoluble, hydrophobic liquid substance. Within this definition there can be wide ranges of surface free-energies and flow characteristics. As shown in Table A (see Appendix), research related to oil sorption by cellulosic materials has included petroleum-derived oils (crude oil, engine oil, diesel fuel, kerosene), natural oils (olive oil, palm oil wastes, *etc*.) and a variety of other oils.

Crude petroleum oils have several different main components that are present in different proportions, depending on the source (Simanzhenkov and Idem 2003; Fingas, 2011b, Silva *et al.* 2011). One way to compare different crude oils is by the fractions that can be collected at different boiling points, while also using boiling under vacuum to collect some of the less volatile components. Thus, crude oils can be described in terms of their contents of such components as light petroleum, heavy naphthene, kerosene, diesel, and vacuum gas oil (Simanzhenkov and Idem 2003). In terms of chemical composition, the main components usually are paraffins (alkanes that can be linear or branched), naphthenes (non-aromatic multi-ring structures), and aromatic compounds. Asphaltenes are a class of compounds that contain paraffin and aromatic structures, as well as heteroatoms such as nitrogen, sulfur, or oxygen (Simanzhenkov and Idem 2003; Varadaraj and Brons 2007a-d; Silva et al. 2011). In practical terms, asphaltenes can be defined as the part of the crude oil that is soluble in toluene but insoluble in simple alkanes such as n-pentane (Natarajan *et al.* 2011). Figure 2 shows some typical structures of each class of compound in crude petroleum oil. Table 5 lists some basic properties of a variety of oils that might be recovered with sorbents (Fingas 2012b,c). Within each class there is a wide range of molecular mass, presence of alkyl branches, *etc.* Based on the research of Varadaraj and Brons (2007a), complexation between nitrogen-containing asphaltenes and naphthenic acids in crude oil can contribute to strong interfacial activity. Asphaltenes appear to affect changes in the physical form and properties of spilled oil over time (Varadaraj and Brons 2007c-d).

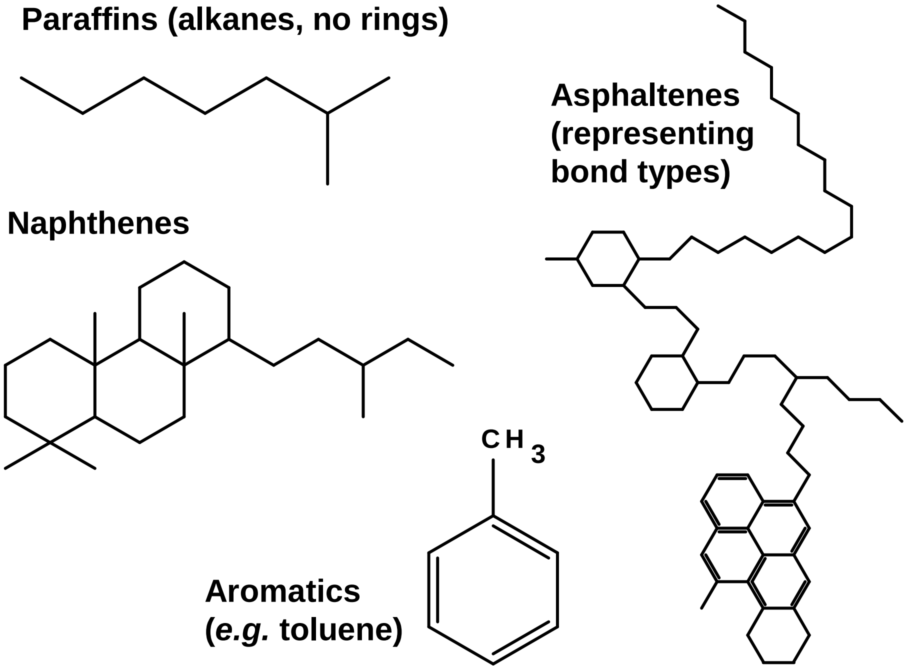

Fig. 2. Representative chemical structures of some components of crude oils (see Simanzhenkov and Idem 2003; Silva *et al.* 2011)

Another type of oil-contaminated wastewater that has received a lot of research attention for its collection is the effluent from olive oil processing plants (Justino *et al.*

2012). Such wastewater exhibits considerable toxicity; examples of some problematic compounds that are found in such wastewater are shown in Fig. 3. Notably, some of these species, *e.g.* syringic acid, are closely related in structure to lignin. Though there has been considerable study of such pollutants (Ena *et al.* 2009; Chouchene *et al.* 2010, 2012; Coz *et al.* 2011; Jeguirim *et al.* 2012; Justino *et al.* 2012), it is still not clear whether the toxic compounds are mainly present as emulsions or in solution in typical cases.

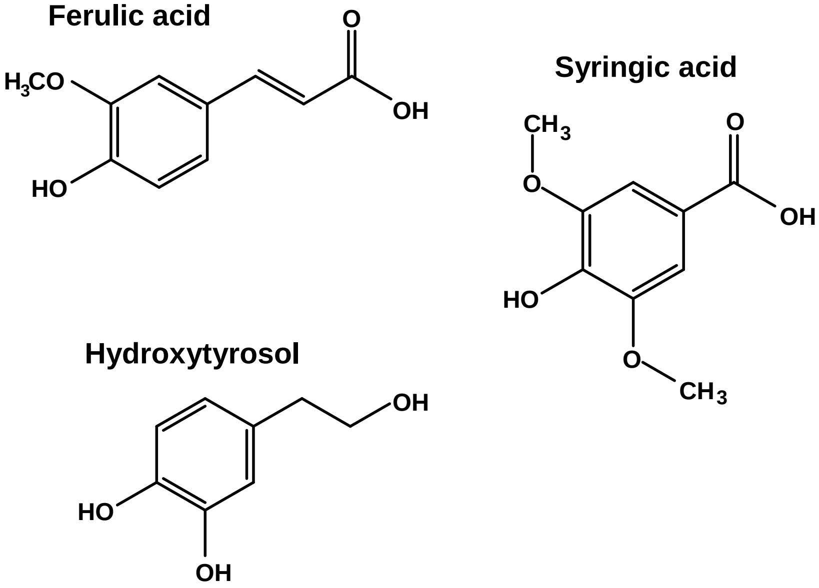

Fig. 3. Some typical phenolic components of effluent from olive oil production facilities (see Justino *et al.* 2012)

Table 5. Typical Oil Properties

Property	Units	Light Crude	Heavy Crude	Heavy Fuel	Olive Oil
Viscosity	mPa.s at 15 °C	5 to 50	50 to 50,000	10,000 to 50,000	50 to 200
Density	g/mL at 15 °C	0.78 to 0.88	0.88 to 1.00	0.96 to 1.04	0.91 to 0.916
Flash Point	°C	-30 to 30	-30 to 60	>100	>100
Solubility in Water	Ppm	10 to 50	5 to 30	1 to 5	<1
Pour Point	°C	-40 to 30	-40 to 30	5 to 20	- 10 to 0
Interfacial Tension	mN/m at 15 °C	10 to 30	15 to 30	25 to 35	30 to 35

Viscosity

The viscosity of a liquid oil, as defined by its resistance to flow, has a critical effect on spreading of oils onto cellulosic materials (Aulin *et al.* 2008). As can be seen from Table 5, the oils for which sorbents might be employed can cover a wide range of viscosities. Generally a low viscosity will favor more rapid sorption (Browers 1982; Perwuelz *et al.* 1999; Hutchinson and Davison 2008; Seveno *et al.* 2011). However, a higher viscosity can be expected to slow the leaching of sorbed oil from the sorbent, after its collection. Substrates having relatively large pores are regarded as promising for sorbing higher-viscosity oils (Rethmeier and Jonas 2003). Fluid viscosity also has been found to be a key factor affecting the performance of "wipe" products (Lee *et al.* 2006).

Interfacial tension

Oils also can differ greatly from one another in terms of the interfacial tension at the oil-air or oil-water interfaces, as noted in Table 4. The oil's surface tension (usually evaluated in air) has been found to govern the rate of spreading onto a cellulosic surface (Browers 1982; Aulin *et al.* 2008). In the case of crude oils, the surface tension is affected by the amounts and chemical nature of its constituents (Buckley 1998; Buckley and Wang 2002; Drummond and Israelachvili 2004). Ghannam (2003) showed that the addition of a surfactant, thus lowering the surface tension, enhanced spreading of crude oil over a hydrophilic limestone surface.

The thickness of a floating layer

The thickness of oil that constitutes a floating layer or "slick" has been specified in various studies dealing with the use of sorbents (Ghaly and Pyke 2001; Hussein *et al.* 2009c; Cojocaru *et al.* 2011, ASTM 2012). Hussein *et al.* (2009c) found that the amount of oil picked up by carbonized bagasse material increased by more than a factor of two as the oil film thickness increased from 1 to 5 mm. By contrast, results of the study by Cojocaru *et al.* (2011) showed that collection became less effective when the thickness of the oil layer exceeded the capacity of the amount of sorbent applied.

State of oxidation/evaporation (time)

Several authors have examined effects of time on the characteristics and recovery of spilled oil on water (Oh *et al.* 2000; Deschamps *et al.* 2003a; Perkovic and Sitkov 2008; Sathasivan *et al.* 2010). In particular, crude oils tend to become more viscous over time due to evaporation of low-molecular-mass components (Oh *et al.* 2000).

State of emulsification

Another way in which the material properties of an oil slick can be transformed over time is through emulsification (NAS 2003; Fingas 2011a). Due to the ubiquitous presence of wave action, but also dependent on the presence and details of surface-active components in the oil (Natarajan *et al.* 2011), it is common for droplets of water to become incorporated into the bulk oil phase, forming W/O emulsions (Fingas 2011a), which are typically highly viscous. Wave action also can promote formation of O/W emulsion droplets, which then tend to be dispersed into the water column. The latter effect can be further promoted by the use of surfactants such as sorbitan oleates (Varadaraj *et al.* 1995a; CRRC 2012).

Aqueous Environmental Properties

A number of investigators have examined the degree to which conditions in an aqueous phase can affect the uptake of floating oil onto a sorbent material. Such results are considered in the subsections that follow.

pH

Several studies have documented significant effects of pH on the wetting of surfaces by oil or on the collection of oil by water-wetted substrates (Dimov *et al.* 2000; Svitova *et al.* 2002; Drummond and Israelachvili 2004; Rajaković-Ognjanović *et al.* 2008; Ibrahim *et al.* 2009).

Dimov (2000) found maximum uptake of emulsified droplets of oil onto glass substrates in cases where the pH was adjusted so as to yield opposite signs of charge on the substrate *vs.* the droplets of oil. For example, in studies carried out in the presence of cationic surfactant, Ibrahim *et al.* (2009) found the highest uptake of emulsified oil onto barley straw when the pH was greater than 4 to 6; such results are consistent with an expected increased sorption of the cationic surfactant molecules onto the more fully dissociated carboxyl groups of the substrate with increasing pH.

Systems close to uncharged conditions also seem to be effective for oil uptake: Svitova *et al.* (2002) adjusted the pH to change the wettability of chitin- and chitosan-treated substrates by silicone oil; the lowest contact angles of the oil on the substrate were achieved under conditions of charge neutrality of the substrate surfaces in each case. Corresponding results were obtained by Varghese and Cleveland (2008), who studied the collection of oil-in-water emulsion droplets onto unmodified kenaf fiber in a deep-bed filter; the highest sorption was found at low pH, which would correspond to protonated, uncharged surfaces of the fiber.

Temperature

Temperature is one of the key parameters affecting uptake of various pollutants onto substrates (Aksu 2005). Rajaković-Ognjanović *et al.* (2008) observed increased uptake of motor oil onto wool-based sorbents with increasing temperature. Haussard *et al.* (2003) likewise observed a rapid increase in oil uptake onto modified bark as the temperature was increased from 10 to 20 ^{o}C, with an additional gradual increase as the temperature was raised further to 50 ^{o}C. By contrast, Suni *et al.* (2007) observed higher capacities of diesel oil collection onto cotton grass at relatively low temperatures.

Coagulants and flocculants

In view of the widespread use of coagulants and flocculants in the primary clarification of water or wastewater (Pushkarev *et al.* 1980; Pokhrel and Viriraghavan 2004; Bolto and Gregory 2007), one would expect that such additives also would play a role in the collection of oil droplets from water onto sorbent materials (Kokal 2002; Simonzhenkov and Idem 2003). However, relatively few investigators have pursued studies involving such treatments.

Zouboulis and Avranas (2000) found little benefit, in terms of separation, from the addition of polyelectrolytes to an O/W emulsion of octane. However, addition of ferric chloride and adjustment of the pH to 6 in the presence of sodium oleate enabled successful separation of the oil by dissolved air flotation.

Salinity

Few studies have considered whether or not ordinary salts might affect collection of oil by cellulose-based materials. Svitova *et al.* (2002) found that whereas monovalent salt ions had little effect, divalent ions such as calcium ion affected the wetting of various substrates by silicone oil. Most of the substrates tested became more hydrophilic in the presence of $CaCl_2$; however, a chitosan-treated surface developed a lower contact angle with silica oil when immersed in $CaCl_2$-containing aqueous solution. Drummond and Israelachvili (2004) found that although ionic strength had some effect on surface interactions between a mica surface (possibly representing cellulose) and oil, more important effects could be attributed to the preferential adsorption of various minor chemical components present within the oil.

THEORIES TO ACCOUNT FOR OIL UPTAKE

This section considers theoretical explanations that have been proposed to account for observed differences in amounts of oils taken up by different sorbents (Table A). Also, there will be an attempt to relate various theories to some of the trends and dependencies described in the previous section. In general terms, much of the theoretical work can be classified based on three main areas: forces of interaction, the contact angles associated with the wetting of surfaces, and the tendencies of liquids to enter into pores. Each of these topic areas will be considered in the subsections that follow.

Intermolecular and Interfacial Forces

Whether or not an oil will spread on the surface of an absorbent material – thus making sorption possible – will ultimately depend on forces at the molecular level. The following types of forces will be considered:

- van der Waals/London dispersion forces (acting between molecules of all types)
- Debye and Keesom forces (polar contributions to van der Waals interactions)
- π-π interactions (acting between aromatic rings present in many common oils)
- Hydrogen bonding (molecules where H is connected to an electronegative atom)
- Hydrophobic effect (water structure changes promoting self-association of oils)
- Double layer forces (when solids or oil droplets have ionic charge in solution)

van der Waals forces

Other than electrostatic and covalent forces, the most important forces between adjacent molecules are due to interactions between permanent rotating dipoles (Keesom interactions), between a permanent rotating dipole and an induced dipole (Debye interactions), and between two induced dipoles (London or dispersion interactions). The dispersion contribution originates from the motion of electrons around the nuclei and is always present. Except for highly polar molecules, it can be shown that the dispersion contribution accounts for nearly all the van der Waals interaction. Oily liquids are not an exception (Visser 1972; Rosenholm 2010). The interaction energy is inversely proportional to the separation distance between the molecules to the power of six.

The van der Waals interactions between two macroscopic bodies can, as a first approximation, be calculated by summing the interactions between all molecular pairs between the two bodies. In practice this is done by an integration (Hamaker 1937), and results of such calculations imply that the distance-dependency of the van der Waals interaction between macroscopic surfaces is much weaker than that between molecules, *i.e.*, the interaction is more long-ranged. Due to the generally nonpolar, non-hydrogen-bonding nature of most oily liquids, one can expect van der Waals forces to play a dominant role in determining their interfacial behavior (Abdullah *et al.* 2010; Hammer *et al.* 2010; Zhu *et al.* 2010). More complete information about van der Waals interactions can be obtained from review articles (Visser 1972; Fröberg *et al.* 1999; Rosenholm 2010).

The magnitude of dispersion forces depends on molecular polarizability and distance. Polarizability means the degree to which the electrons of an atom or molecule are susceptible to being pushed. In general, it is the electrons in the outermost electronic shell that are largely responsible for the polarizability of a given atom or molecule. It so happens that the electrons present in saturated alkanes, which are predominant in many common hydrocarbon oils, have only a modest degree of polarizability (Wennerstrom 2003). In other words, the Hamaker constant governing the London dispersion component of the van der Waals force in the case of simple alkane oils is relatively low, *e.g.* 5.8 x 10^{-20} J (Visser 1972). The same source lists various aromatic liquids as having much higher Hamaker constants, generally in the range of 10 to 60 x 10^{-20} J. This is important because, as was noted earlier, most crude oils contain substantial quantities of aromatic compounds in addition to paraffin-like hydrocarbons (Simanzhenkov and Idem 2003). Zhu *et al.* (2010) have asserted that the polarizabilities of solids and liquids can be expected to play a major role with respect to contact angles and wettability.

The two other components of van der Waals forces – the Debye and Keesom components – can be expected to be important when an impure oil phase is interacting with a polar phase, *e.g.* water or cellulose. The Debye component of force results when polar molecules induce transient dipoles in nearby nonpolar molecules (Roberts and Orr 1938), and the resulting force tends to be greater than the dispersion component of force. It follows that the Debye component of force will contribute to the spreading of oil onto cellulosic substrates, and that the magnitude of the contribution will be greater if the oil contains a lot of the relatively polarizable aromatic groups, as well as sulfur-containing groups.

The component of van der Waals forces called the Keesom force arises from the interactions between pairs of molecules that have permanent dipoles (Hiemenz and Rajagopalan (1997). According to Pasichnyk *et al.* (2008) the Keesom force sometimes can be important when an oil phase that contains polar molecules interacts with a water phase. Although an individual dipole-dipole interaction can greatly exceed the energy of a corresponding London dispersion interaction, considerably fewer polar molecules are present in a typical oil phase compared to nonpolar molecules, the latter of which can interact mainly by the London dispersion and Debye components of force.

π-π stacking

Two explanations have been given to account for the higher contribution of aromatic groups to the dispersion component of interactive energy. First, it has been proposed that because the aromatic rings provide for greater freedom of motion of certain electrons (Hiberty and Shaik 2005), a higher polarizability can be expected (Zeinalipour-Yazdi and Pullman 2006). The second explanation is based on a more specific interaction between adjacent aromatic rings. When such rings are stacked face-to-face, a substantial component of bonding can be expected due to π-π interactions, again involving the aromatic ring electrons (Walters 2002). Because crude oils generally contain both aromatic and aliphatic hydrocarbons, it is reasonable to expect that contributions will come from both of the mechanisms just described.

π bonding is also expected to significantly contribute to interaction between an oil phase and substances that have ionic charges. For instance, cations (which could be present in an aqueous solution or on a cellulosic sorbent surface) have been shown to interact with π electrons, giving rise to an attraction (Mahadevi and Sastry 2012; Lu *et al.* 2013). Frontera *et al.* (2011) have reviewed the subject of π bonding interactions with cationic and anionic groups. The cited authors note that this component of interactive forces can be used to fine-tune the calculations of interactive forces, even though the π interactions with charged groups is typically less important than hydrogen bonding (see later). The contribution of π electrons of aromatic groups, during interaction of oils with water, has been reviewed (Furutaka *et al.* 2001).

Greater dispersion forces also can arise if an oil contains polarizable atoms such as sulfur. This element is often present in crude oils in the form of thiophenes (Kropp and Fedorak 1998; Samokhvalov 2011). As noted by Moellmann and Grimme (2010), sulfur substitution on aromatic groups within oil can be expected to influence π-π stacking.

Although "nonpolar nature" is often regarded as a defining feature of an "oil" (Simanzhenkov 2003), many common oils also contain polar species to some degree. Such molecules can contribute not only to the internal cohesion of the oil but also to its spreading onto various surfaces.

Hydrogen bonding, water structure, and the hydrophobic effect

Hydrogen bonding can play an important role in the spreading of oil onto water-wet substrates, particularly in the case of cellulosic sorbents. That is because cellulosic materials have substantial ability to hydrogen bond at their interface with an aqueous phase. By contrast, the nonpolar molecules in oil cannot form hydrogen bonds at the interface with water. This difference helps to explain why lower amounts of oil uptake sometimes have been observed on water-wetted cellulosic fibers in comparison to dry fibers of the same type (Payne *et al.* 2012). Nonpolar substances in water induce changes in the liquid water structure. In this case the water molecules rearrange themselves in the vicinity of the solute to maximize the number of water-water hydrogen bonds. This change in water structure is the basis for the hydrophobic effect that drives self-assembly of nonpolar entities in liquid water (Meyer *et al.* 2006). Overall, it can be stated that hydrogen bonding is an important factor in aqueous systems carrying solutes and surfaces (Claesson *et al.* 2006). Some useful background regarding hydrogen bonding and its relationship to phase interactions can be found in the following sources (Jacob and Berg 1993; Good *et al.* 1996; Tze and Gardner 2001; Dill *et al.* 2005; Claesson *et al.* 2006; Eriksson *et al.* 2007; Djikaev and Rubenstein 2011).

Though each pyranose unit of a cellulose or hemicellulose macromolecule contains three –OH groups, only a fraction of such groups are available to participate in hydrogen bonding with an aqueous phase under ordinary conditions (Mann and Marrinan 1958; Kadla and Gilbert 2000). As a consequence, a typical cellulosic surface is not fully hydrophilic (Biermann *et al.* 2001). Indeed, certain crystal faces of cellulose actually can be regarded as being hydrophobic. The work of Yamane *et al.* (2006) substantiates this principle, showing that it is possible to manipulate the number of –OH groups exposed at the cellulose surface by regeneration of cellulose in the presence of different liquids.

The hydrophobic effect, as mentioned above, may also help explain the enhanced performance of naturally wax-coated or alkylated cellulosic materials, as described earlier (see, for instance Choi and Cloud 1992; Raible 1990; Lim and Huang 2007b; Payne *et al.* 2012). Thus, in addition to the van der Waals attraction promoting such spreading of oil onto the substrate surfaces, the association of oil with the substrate also tends to decrease the net area of oil-water interface in the system. Reduced oil-water interfacial area implies that more of the water molecules behave as bulk water, a state that is thermodynamically preferred due to the greater degrees of freedom of such molecules. In addition, the presence of micro/nano-scale bubbles of air has been shown to extend the apparent distance over which the hydrophobic effect can operate (Meyer *et al.* 2006; Faghihnejad and Zeng 2012).

Electrostatic (double layer) forces

A solid-aqueous solution interface is most often charged due to one of several mechanisms; acid–base equilibria, desorption of lattice ions as in the case of clays and minerals, or adsorption of ionic surfactants, multivalent ions, and polyelectrolytes. The surface charge is exactly balanced by the net charge in the solution outside the surface (Hiemenz and Rajagopalan 1997). In the region immediately outside the surface, say less than 1 nm from the surface, the ions may, in addition to electrostatic forces, experience other interactions with the surface. These ions are said to be adsorbed, and they build up the so called Stern layer. Outside the Stern layer, in the diffuse layer, the ions are only affected by electrostatic forces, and in this region it is straightforward to calculate the ion concentration away from the surface. The effective distance that the diffuse layer extends from a surface will depend on the concentrations and valencies of ions in solution. A central quantity in this respect is the Debye length, which describes the rate with which the mean potential decays away from the surface. The Debye length decreases with increasing ionic strength, but it is independent of the surface charge density and surface potential. An electrostatic double-layer force arises when two surfaces come close enough for their diffuse layers overlap to an appreciable extent.

Wang *et al.* (2012) recently demonstrated the influence of the double layer in governing the forces between mineral (mica) surfaces in an aqueous system with the presence of a surfactant having characteristics similar to the asphaltene component of crude oils. Because asphaltenes are enriched at the surfaces of oil phases (Natarajan *et al.* 2011), such a system is highly relevant to the collection of crude oil onto a sorbent material. As would be expected based on double layer interactions, the forces between the surfaces coated with the model asphaltene molecule were greatly affected by changes in pH, monovalent salt concentration, and especially by Ca^{2+} ion addition (Wang *et al.* 2012). These results are generally in agreement with those by Svitova *et al.* (2002), as mentioned in the earlier discussion of aqueous environmental properties.

Interactions between phases

Whether an oil phase will spread onto a sorbent surface and ultimately permeate into pores of the solid, will depend on forces of interaction across phase boundaries. To a first approximation, the forces of interaction between adjacent phases can be regarded as given by a summation of quasi-independent forces described in the preceding subsections (Fowkes 1964). The following equation illustrates this concept.

$$F_{\text{net}} = F_{\text{electrostatic}} + F_{\text{hydrogen bonding}} + F_{\text{van der Waals}} \tag{1}$$

In this expression each of the terms is assumed to be independent and non-overlapping. Rosenholm (2010) examined possible errors resulting from such an approach, with a focus on van der Waals components; it was concluded that such models tend to oversimplify real systems – in particular by not taking into account effects due to impurities and the overlapping nature of different mechanisms of interaction between molecules. Future studies also need to consider whether or not it is useful to include the hydrophobic effect, mention earlier, as a term in Eq. 1.

Contact Angles and Wetting

Although the topic of wettability of solids by liquids has been well described elsewhere (Fowkes 1964; Adamson and Gast 1997), there are certain aspects that merit emphasis in the context of sorption of oils. Table 5 lists some key concepts, together with selected literature citations.

Table 6. Factors Affecting the Wetting of Cellulosic Substrates by Oils

Concept	**Selected References**
The low free energy of the oil surface provides a driving force for it to get out of a water phase and into some other phase, *e.g.* adsorbed on a surface.	Adamson & Gast 1997
The relatively high free energy of a typical cellulosic surface provides a driving force for the spreading of most liquids (especially in the absence of water).	Adamson & Gast 1997; Roman 2009
Roughness and chemical heterogeneities of cellulosic substrates can be expected to cause hysteresis effects. Thus, there will be an extra resistance to initial wetting, but once a surface has been wetted, it is then hard to retract the liquid and "de-wet" the surface.	Johnson and Dettre 1969; Roman 2009
The presence of small pores in a cellulosic substrate can be expected to result in relatively large hysteresis effects (see previous item).	Cassie & Baxter 1944; Denesuk *et al.* 1994
The presence of water on a cellulosic surface may lead to significant swelling of the material, thus providing more volume of pores that can affect wetting and accommodate oil.	Payne *et al.* 2012
The presence of water on a cellulosic surface does not necessarily impede spreading of oil on that surface.	Payne *et al.* 2012

Oil contact angles and wetting in the absence of water

In the following simplified description it will be assumed that the surface to be wetted is smooth, planar, non-porous, and uniform in composition. Also, for the first case, the surface will be assumed to be water-free and in contact with ambient air. The test liquid, *i.e.* the "oil", will be assumed to be a pure compound. In such a case the contact angle can be described by the Young equation (Young 1805; Adamson and Gast 1997),

$$\gamma_{\text{SA}} = \gamma_{\text{SO}} + \gamma_{\text{OA}} \cos\theta \tag{2}$$

where γ_{SA} is the interfacial tension between the solid and air, γ_{SO} is the interfacial tension between the solid and oil, γ_{OA} is the interfacial tension between the oil and the air, and θ is the angle of contact at the three-phase boundary, drawn through the oil. These forces are illustrated in Fig. 4 (Hubbe *et al.* 2012b). As shown in the figure, at equilibrium the three vector quantities must sum to zero, when considering the interfacial tensions acting in the plane of the surface. When the angle θ is less than 90°, the fluid will spread, and the surface will be considered "wettable." By contrast, when θ is greater than 90° the fluid will resist spreading, and the surface is defined as "non-wettable" by the fluid. A relatively low (wettable) contact angle is depicted in Fig. 4, to be consistent with experimental findings (Payne *et al.* 2012).

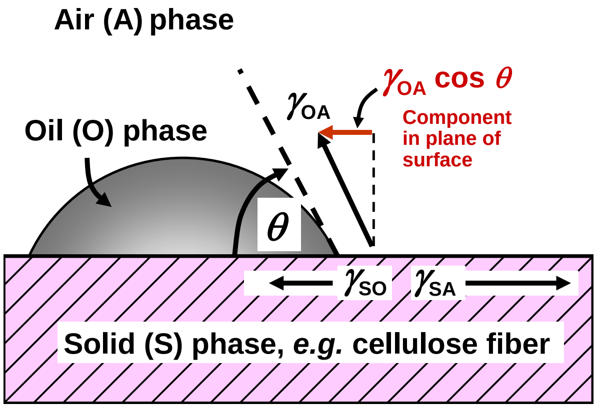

Fig. 4. Definitions of terms in Young's equation, describing the balance of interfacial tensions in the plane of the surface when a droplet of oil is placed on a solid "S" in the presence of air or vapor (A)

Both the spreading of a liquid on a flat surface and the permeation of a liquid into a porous material having the same chemical nature are favored by a low value of θ (Adamson and Gast 1997). Strategies to achieve this condition can be predicted by rearranging Eq. 2 as follows (Hubbe *et al.* 2012b):

$$\cos\theta = [\gamma_{SA} - \gamma_{SO}] / \gamma_{OA} \quad (3)$$

$$\theta = \arccos \{[\gamma_{SA} - \gamma_{SO}] / \gamma_{OA}\} \quad (4)$$

In addition to the surface energy terms already defined above, researchers have found it useful to use the critical surface tension γ_c of a solid surface, as was introduced in previous sections (Fox and Zisman 1952; Fox *et al.* 1955; Zhu *et al.* 2010). The value of γ_c is determined for the desired solid with a set of homologous fluids that have different surface tensions, γ_L. The cosine of the measured contact angle is plotted against the fluid surface tension. Extrapolation of the curve to $\cos\theta = 1$ identifies the value of γ_c for the solid. The concept of critical surface tension implies that a fluid of the series with a surface tension less than γ_c, *i.e.* $\gamma_L < \gamma_c$, will rapidly wet the surface.

More research needs to be carried out in which the concepts of contact angle or critical surface tension are applied to evaluate the spreading behavior of various oils onto cellulose-based surfaces. Aulin *et al.* (2008) found a strong correlation between the dispersive component of free energy and the spreading of oils onto fluorinated cellulose surfaces; a degree of fluorination sufficient to reduce the value of the dispersive component to below 18 mNm^{-1} was needed in order to prevent spreading of castor oil. Payne *et al.* (2012) found that treatments of dry cellulose film to make it more hydrophobic increased the contact angles for both water and crude oil.

Oil contact angles and wetting with oil in the presence of water

Many oil spills take place in the presence of water. In order to make realistic predictions in such cases, the model needs to be changed, as illustrated in Fig. 5.

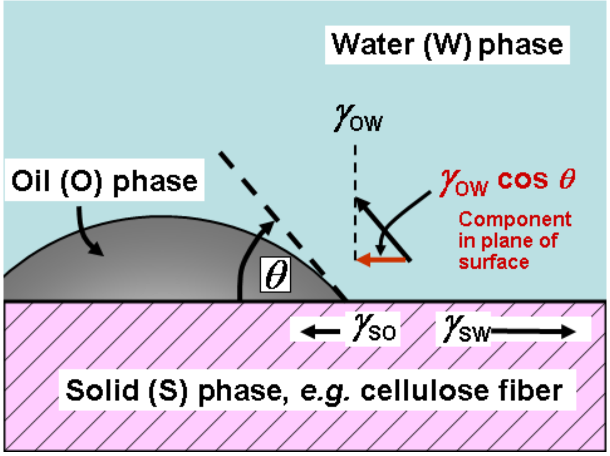

Fig. 5. Definitions of terms in Young's equation, describing the balance of interfacial tensions in the plane of the surface when a droplet of oil is placed on a solid "S" in the presence of water (W) or aqueous solution

All of the relationships associated with Fig. 5 are analogous to those already expressed in Eqs. 3 through 4, *i.e.*,

$$\cos\theta = [\gamma_{SW} - \gamma_{SO}]/\ \gamma_{OW} \qquad (5)$$

$$\theta = \arccos\ \{[\gamma_{SW} - \gamma_{SO}]/\ \gamma_{OW}\} \qquad (6)$$

The reason that a somewhat different contact angle is depicted in Fig. 5, compared to Fig. 4, is that the presence of water has been found to actually enhance the tendency of oil to wet a cellulose-based substrate (Payne *et al.* 2012). This effect needs to take into account hydrogen bonding interactions occurring at the boundary between the sorbent surface and the aqueous solution (Vogler 1998; Yamane *et al.* 2006). Such interactions would tend to decrease the value of the γ_{SW} term because the partially hydrogen bondable cellulosic phase is facing water. Meanwhile, the value of the γ_{OW} term typically would be somewhat lower than that of γ_{OA} due to significant London dispersion interactions expected between the oil and aqueous phases (and almost no such interaction with air). Regarding the γ_{SO} term, the cited results of Payne *et al.* (2012) suggest that its value also decreases, consistent with an observed lowering of the contact angle on cellulose film surfaces that were saturated with water. However, further study is needed in order to more fully understand what is happening at such phase boundaries.

Hysteresis Effects

Before applying the above relationships to draw inferences about absorption of liquids into pore spaces, some details related to hysteresis need to be emphasized. In other words, under realistic conditions there are various factors that tend to inhibit the initial wetting of a surface, but which also tend to resist "retraction" of liquid from a surface after wetting has taken place (Perwuelz 1999).

Effects of surface roughness

The inherent roughness and heterogeneity of real surfaces can affect contact angles and wettability in two different ways, one of which does not involve hysteresis. The equilibrium effect – which is generally associated with very fine scales of roughness – was first modeled by Wenzel (1936). This author noted that the true area of a real surface is always greater than that of a smooth geometrical plane representing the same object. To account for this fact, the amount of interactive energy involved in the spreading of a liquid needs to be multiplied by a factor *r*, representing the ratio between the true (rough) wettable area and that of a plane or smoothly curved surface drawn in place of the true surface. Thus, for example, Young's equation for the contact angle of oil on a dry (but rough) surface should be re-written as follows:

$$r\,\gamma_{SA} = r\,\gamma_{SO} + \gamma_{OA}\cos\theta, \quad \text{or} \tag{7}$$

$$\gamma_{SA} = \gamma_{SO} + (\gamma_{OA}\cos\theta)\,/\,r \tag{8}$$

In addition to the effects predicted by Wenzel (1936), a rough surface can give rise to non-equilibrium effects, especially if the features or roughness are large relative to the size of the meniscus. A mechanism to account for such effects was proposed by Johnson and Dettre (1969). As illustrated in Fig. 6, one can imagine a droplet resting on the surface of a rough, tilted nonporous substrate. The roughness is represented as having a pronounced "staircase" or "wavy" shape. In more recent work Hejazi and Nosonovsky (2012) also considered a shingled or "fish-scale" morphology of a surface to be wetted.

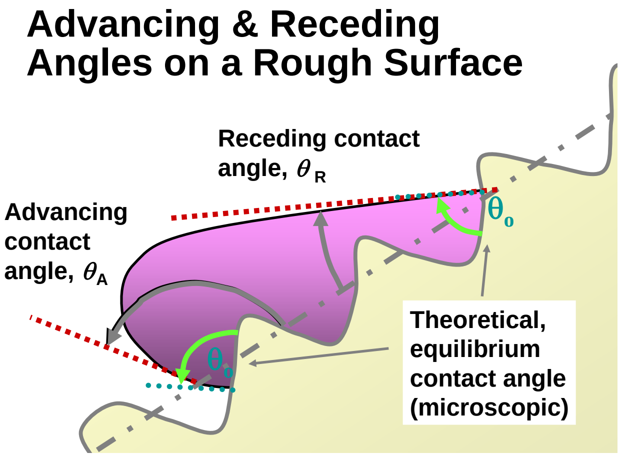

Fig. 6. Comparison of macroscopic and microscopic contact angles on a hypothetical inclined rough surface and a droplet of fluid

In Fig. 6 the angle of tilt has been chosen such that the lower edge of the droplet can represent an advancing contact angle, and the higher edge of the droplet can represent a receding angle. As shown in the figure, the macroscopically observed angles can be expected to show a large difference between the leading and trailing edges of the droplet. However, if one were to microscopically observe the angles of contact, relative to the local features of the surface, then it is likely that all of the observed angles would be the same, supporting the use of a single value, as in the Young equation (Oliver *et al.* 1977).

Chemical inhomogeneities can have effects on contact angles that are analogous to those of physical roughness. Thus, alternate patches of hydrophobic and hydrophilic character on a surface have been shown to result in large differences between the advancing and the receding contact angles (Johnson and Dettre 1969; Neumann and Good 1972; Rodriguez-Valverde *et al.* 2008). Such effects can be particularly evident in the case of water droplets. The advancing of such droplets tends to be resisted by hydrophobic patches of surface, which offer weak interaction, whereas the retraction of such droplets tends to be resisted by relatively strong interactions with hydrophilic patches of surface.

Effect of fine-scale porosity

A mathematical relationship to account for hysteresis effects of contact angles on porous surfaces was derived by Cassie and Baxter (1944). These authors noted that during the initial wetting of a surface the voids present do not contribute any component of attractive force on the approaching liquid phase. By contrast, it follows that once the surface has been wetted, such pores will tend to remain filled with liquid, contributing the interfacial force. This situation is illustrated in Fig. 7. In particular, if the surface is otherwise homogeneous (except for the presence of pores), then the following correction to the advancing contact angle can be applied,

$$\cos \theta_{a,p} = f_1 (\cos \theta) - f_2 \tag{9}$$

where $\theta_{a,p}$ is the advancing angle on a porous surface, f_1 is the area of wettable solid as a fraction of the planar area, and f_2 is the fractional open area (sum of pore cross-sections) relative to the planar area.

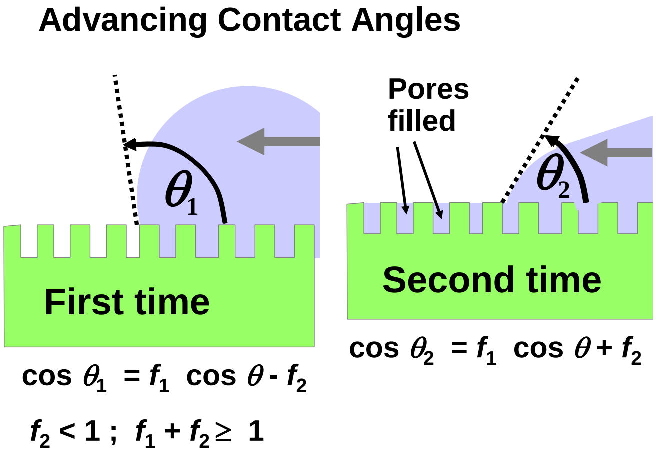

Fig. 7. Implications of Cassie and Baxter's theory relative to a first and second wetting of a porous surface

Because the surface may be rough, the sum of f_1 and f_2 may exceed the planar area. In this way, Cassie and Baxter (1944) are able to include Wenzel's result (see above) as a limiting case when there are no pores on a surface. A recent article by Milne and Amirfazal (2012) provides detailed guidance on the use of Eq. 9 and its applicability to prediction of wetting phenomena in practical cases. According to McHale (2007), the validity of the Cassie and Baxter and Wenzel equations extends even to the wetting of superhydrophobic surfaces, as long as one pays close attention to local details near to 3-phase lines of contact.

Absorption into Porous Solids

Various authors have proposed that "capillary action" is a key mechanism by which oil is taken up by sorbent materials (Choi *et al.* 1993, 1994; Ribeiro and Rubio 1999; Ribeiro *et al.* 2000; Inagaki *et al.* 2002b; Al-Marzouqi *et al.* 2003; Haussard *et al.* 2003; Lim and Huang 2006; Cojocaru *et al.* 2011; Diersch *et al.* 2010; Masoodi *et al.* 2010, 2011; Carrillo *et al.* 2012). In other words, contact angle phenomena govern the wicking of oils into porous substrates. The subject of the capillary action of absorbents has been reviewed by Chatterjee and Gupta (2002).

Dry porous solids

The values of γ_{OA}, contact angle, fluid viscosity, and the characteristic pore size can be used to estimate the effect of time on the sorption of a fluid into void spaces between particles or fibers in a sorbent material. These relationships are illustrated in Fig. 8, which corresponds to the Lucas-Washburn equation when considering an initially dry sorbent material (Lucas 1918; Washburn 1921). Several investigators have reported good agreement of the Lucas-Washburn model with observed rates or extents of sorption of oils into porous materials (Gupta 1988; Al-Marzouqi *et al.* 2003; Gane 2004; Brugnara *et al.* 2006; Hutchinson and Davison 2008; Masoodi and Pillai 2010; Masoodi *et al.* 2010).

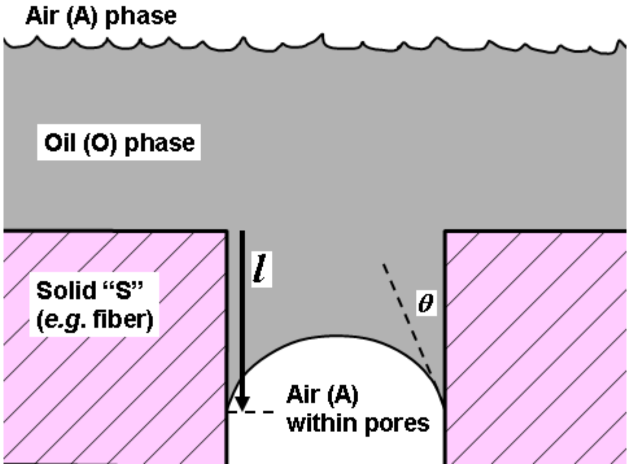

Fig. 8. Lucas-Washburn model of penetration into an idealized pore of a dry sorbent

In the equations given below, governing the permeation of fluid into pores, the variable l is the distance that liquid has permeated within a period of time t, when the fluid has a viscosity η.

$$\mathrm{d}l / \mathrm{d}t = \gamma_{\mathrm{OA}} R \cos \theta / (4 \eta l) \tag{10}$$

$$l = [\gamma_{\mathrm{OA}} R t \cos \theta / (2 \eta)]^{0.5} \tag{11}$$

The model has been successfully applied for characterizing the linear flow rate (cm/sec) along a strip of fabric hung vertically or laid horizontally (Chatterjee and Gupta 2002). The same author has also applied the Lucas-Washburn equation in developing a model for characterizing the volumetric flow rate (rate of absorption) of fluid in a nonwoven fabric (Gupta and Hong 1995):

$$Q = \frac{\pi R \gamma \cos\theta}{2A\eta}\left[\frac{TA}{W} - \frac{1}{\rho}\right] \tag{12}$$

In Equation 12, using the cgs system of units, Q is the volumetric flow rate (cm^3/g-sec), R is the pore radius (cm), γ is the fluid surface tension (dynes/cm), θ is the contact angle (radians), η is the fluid viscosity (dynes.sec/cm^2), ρ is the density of the fiber material (g/cm^3), and T, A, and W are, respectively, the thickness (cm), planar area (cm^2) and weight (g) of the fabric specimen on which the test of absorbency is conducted. The surface tension notation used is general and should apply to both water-air (γ_{WA}) and oil-air (γ_{OA}) interfacial values. The value of pore size R, which is difficult to measure experimentally, was also modeled and given by the following expression (Gupta 1988):

$$R = \left[\frac{d}{2\pi B_0}\left\{\frac{TA}{W} - \frac{1}{\rho}\right\}\right]^{1/2} \tag{13}$$

In this expression, d is the linear density of the fiber of which the nonwoven fabric is constructed and B_0 is a constant, the value of which depends on the base length associated with the linear density d. If d is the denier of the fiber, then the value of the constant will be (9 x 10^5). Fabrics often contain a blend of two or more fibers or fibers and an adhesive. Modifications have been presented for the models mentioned above to apply to such complex structures (Chatterjee and Gupta 2002, pages 33-50).

In the above two equations (12 and 13), the quantity enclosed within the square (12) or middle (13) brackets, represents the void or air volume per unit mass (cm^3/g) of the specimen. It provides a measure of the absorbent capacity of the bat. Accordingly, one sees that absorbent capacity (cm^3/g) for a given fabric is primarily determined by the thickness per unit mass of the fabric, which represents the bulkiness of the structure. Equation 13 shows that pore size is given by both the air volume per unit mass (absorbent capacity) and the size of the constituent fiber (denier): an increase in either gives an increase in pore size. And now, referring to the model for the absorbency rate (Eq. 12), it becomes clear that for a given fluid and fiber material, an increase in fabric thickness per unit mass and or fiber size leads to a more rapid absorption of fluid. Factors that enhance the voluminous nature of a fabric provide an advantage in terms of both the capacity and the rate. Additionally, selecting fibers of larger size can be expected to improve performance.

Other considerations will be related to the influence that the values of the contact angle and the interfacial tension can have on performance. More specific to the absorption of oil, manipulation of the surface tension, γ_{OA}, can be interesting for a number of reasons. First, the only practical way to change the value of γ_{OA} of spilled oil would be to apply surface-active agents. When released into the environment, such agents can be harmful (Chapman *et al.* 2007; Berninger *et al.* 2011). In addition, surfactant use would be expected to decrease the value of γ_{OA}, thus decreasing the capillary force available to draw the oil into the substrate. Though the contact angle of oil on a dry substrate typically has a low value (Payne *et al.* 2012), it is reasonable to expect that the contact angle could be changed up or down by a surfactant, depending on the molecular structure and hydrophile-lipophile balance (Adamson and Gast 1997).

As already discussed, the models (Equations 11 and 12) suggest that to maximize the rate of sorption of oil into dry sorbent, the pore size should be maximized. Such a strategy would be consistent with the results of various empirical studies that were summarized earlier in this article. Large pore size has been particularly recommended in the case of viscous oils (Browers 1982; Ribeiro *et al.* 2000). Hutchinson and Davison (2008) showed that the rate of oil sorption into paper can be used as a relative measure of the viscosities of different oils. However, a practical constraint is imposed by the need to avoid release of the oil, which is likely to be important for low-viscosity oils. Narrower pores will tend to maintain higher capillary pressures, helping to avoid unplanned release of the sorbed fluids.

Another approach to enhance oil sorption involves chemical treatment. As already discussed, many investigators have treated cellulosic substrates with hydrophobic agents in an effort to make them more suitable for collection of oils (Ball 1973; Maurin *et al.* 1999; and many others). However, as reported by Payne *et al.* (2012), such an approach does not aid in the sorption of oils onto dry cellulosic material. Rather, the amounts of sorbed oil may be reduced by such treatment. Such effects are consistent with an expected increase in the value of θ for a given liquid when the surface has been treated to reduce its free energy (Adamson and Gast 1997).

Displacement of water by oil

Figure 9 considers the corresponding situation when a water-saturated, porous substrate is used to collect oil. Note that this figure is almost identical to Fig. 8 except for some of the labels. Also, the contact angle is drawn somewhat differently, in recognition that the presence of water may affect the value, and such a change will not necessarily be favorable for sorption of the oil (Svitova *et al.* 2002; Said *et al.* 2009; Payne *et al.* 2012). Due to van der Waals interactions at the oil-water interface, compared to their relative absence at the air-water interface, it is expected that $\gamma_{OA} > \gamma_{OW}$. Thus, if one assumes that the substrate is exactly the same in Figs. 8 and 9, and if the respective contact angles are all quite low, as observed by Payne *et al.* (2012), then this factor would cause one to predict that the dry substrate will pick up more oil in a given time. However, another key difference relative to the situation depicted in Fig. 8 is that the viscosity term corresponding to Fig. 9 can be expected to be greater and more difficult to quantify. When aqueous fluid is initially present in the pores of a substrate, flow of oil entering the system will be impeded not only by the viscosity of the oil, but also by the viscosity of the water, and a final term needs to be added, as shown in Eq. 14, where the terms η_O and η_W correspond to the dynamic viscosity of the oil and the water, respectively, and the terms l_O and l_W correspond to the lengths of typical capillary channels wetted by oil and by water, respectively.

$$dl / dt = \gamma_{OA} R \cos \theta / (4 \eta_O l_O + 4 \eta_W l_W) \tag{14}$$

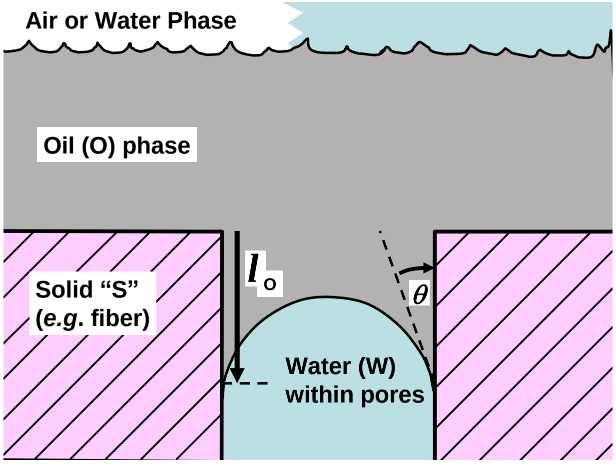

Fig. 9. Lucas-Washburn model of penetration of oil into an idealized pore of a water-wet sorbent

By applying a hydrophobic treatment to the substrate it is possible to achieve a substantial reduction in the contact angle of oil on the water-wetted substrate. This can be done, for instance, by treating cellulosic fibers with a sizing agent such as alkenyl-succinic anhydride (ASA) (McCarthy and Stratton 1987; Wasser 1987; Hodgson 1994; Payne *et al.* 2012). The resulting incompatibility between the treated fibers and water implies that the value of γ_{SW} will be higher than it would have been for untreated fibers. Increased oil-wettability and sorption are expected. This helps to explain the results of Payne *et al.* (2012), who found that hydrophobization of a cellulose surface tended to increase the uptake of oil, when tests were done under wetted conditions. Increased sorption of oil onto water-wet cellulose fibers was observed if the fibers had been treated with either ASA or lignin to make them more hydrophobic. Likewise, Said *et al.* (2009) found that whereas acylated bagasse was especially effective for sorption of oil under water-wet conditions, untreated bagasse had excellent oil-sorption characteristics only in the absence of water. Nduka *et al.* (2008) likewise found that untreated coconut coir, a relatively hydrophilic material, was effective for "on shore" sorption of oil, whereas more hydrophobic materials were more suitable for collection of oil in the presence of water. Witka-Jezewska *et al.* (2003) found that oil spread readily on the surface of wet barley straw, which was found to have a thin waxy layer on it.

Transfer of oil from one porous solid to another

Cojocaru *et al.* (2011) considered the possibility of transfer of oil from one particle of sorbent to another after its initial collection. Such transfer might be important, for instance, if some of the sorbent material becomes oversaturated with oil, while at the same time there is other sorbent material present (perhaps added later) that still has potential to take up oil. The researchers showed that even under water-wet conditions, oil can be wicked from oil-filled peat particles to unfilled peat particles. Two characteristics are necessary for accomplishing such transfer: intimate contact between the saturated and the freshly-added sorbent particles, and finer capillaries in the latter. The capillary pressure, given by the Laplace model, $2\gamma \cos \theta / R$, indicates that the finer the capillaries, the stronger the pull. When the amount of fluid is limited, as is the case when it is contained within the pores of a sorbent, the add-on structure must exert greater pressure to pull it than the pressure holding it in the first material. This process also allows the latter, now partially desaturated, to collect more oil from the spill. For a given fluid and fiber material, the geometry of the sorbent governs the role of collecting and distributing the absorbed into the product. For optimum performance, the structure should allow an efficient transfer of fluid from the point of collection into the capillary network extending throughout the product. Use of channeling and of graded capillary sizes are potential considerations that require more research.

Dynamic wettability effects

The subject of time-related effects has been left almost to the end of this discussion due to the fact that many applications of sorbent technology involve relatively long periods of time, possibly sufficient for equilibrium conditions to be established. But that will not necessarily be the case if, for instance, contaminated water is passed rapidly through a bed of sorbent material (Deschamps *et al.* 2003b). Considerable efforts have been made in recent years to understand the factors governing contact angles under non-equilibrium conditions (Gouin 2001, 2003a,b; Seveno *et al.* 2011). In general, flow-related resistance to spreading of oils can be expected to reduce the amount of sorption during short-term exposure in comparison to that resulting from long-term exposure, approaching equilibrium uptake.

STRATEGIES TO COLLECT OIL WITH CELLULOSIC SORBENTS

This section considers ways to deploy cellulosic sorbent materials to deal with realistic situations involving the spillage of oily liquids in the presence of water. In a broad sense the options include using the sorbents as a deep-bed filter, spreading the sorbent on top of an oil slick, or incorporating the sorbent in a floating boom or other such structure. Each one of these general strategies has implications concerning such variables as particle size, packing density, ability to float, and other attributes of the sorbent material.

Using the Sorbent as Filter Media

Filtration of oil-contaminated water through cellulosic media can make sense in cases where the oil is dispersed as emulsion droplets, as well as larger droplets, lenses, or a sheen of oil at the air-water interface. The discussion that follows will be divided into deep or packed bed filtration and membrane filtration.

Packed beds

In a packed bed system the sorbent material is held stationary while the contaminated stream is passed through it. Theoretical issues related to the collection of oil onto packed beds have been considered by various authors (Lee and Han 1993; Sun *et al.* 1999; Briscoe *et al.* 2000). Some potential advantages of using a packed bed approach to water decontamination include compactness, neatness, and the fact that the sorbent material does not need to be collected, since it is not ever released (Pasila 2004). Factors that have been found to be especially important with respect to oil collection onto packed beds include surface area, effective pore sizes between and within particles in the bed, the void volume, flow rate, and the hydrophobic or hydrophilic nature of the surface (Lee and Han 1993; Briscoe *et al.* 2000; Dimov *et al.* 2000; Palisa 2004; Varghese and Cleveland 2008).

Demulsification in packed beds and membranes

Though sorption has been the main focus of packed bed systems for dealing with spilled oil, there also have been some studies directed at the breaking up of emulsions by passing them through packed beds or filtration membranes. A membrane can be defined as a thin film or fabric that has relatively little capacity for taking up and retaining a sorbate such as an oil. Typically, hydrophobic filtration membranes can be used for demulsification of O/W emulsions due to coalescence of oil droplets in the membrane pores, while hydrophilic membranes can be used for the demulsification of surfactant-stabilized W/O emulsions. The separation process is not based on sieving effects but is determined by droplet interactions with the surface of the membrane. In other words, demulsification is dependent on the type of emulsions and membrane used. Preferential surface wetting allows separation of the phases via ultrafiltration and microfiltration membranes. The effectiveness of cellulose-based membranes in the cleaning up of oil-contaminated water has been demonstrated in a number of studies (Zaidi *et al.* 1992; Hlavacek 1995; Koltuneiwiz and Field 1996; Tirmizi *et al.* 1996; Hong *et al.* 2002; Zou *et al.* 2003; Li *et al.* 2009; Wang *et al.* 2010).

When membranes or fibers are used in dealing with oil-contaminated water, the goals of the operation also may include exclusion of one of the phases from passing through the material. Factors that can influence the efficiency of such separations include the material's hydrophilic or oleophilic nature, the pore size, the applied pressure, and the velocity of cross-flow, *etc*. (Kotuneiwicz and Field 1996; Tirmizi *et al.* 1996). The following authors found that hydrophobized cellulosic fibers were able to selectively remove oily emulsion droplets from aqueous solution (Sun *et al.* 1999; Ribeiro *et al.* 2001, 2003; Rattanawong *et al.* 2007; Ibrahim *et al.* 2009; Wang *et al.* 2010). In the case of membranes, hydrophobic, or hydrophobically-treated materials have been found to permit passage of only the oil portion of an O/W emulsion, while also causing coalescence of oil droplets as they pass through (Hong *et al.* 2002).

Li *et al.* (2009) showed that a hydrophilic membrane could be used to recover emulsified linseed oil droplets from a water phase; the oil droplets were shown to coalesce due to concentration polarization at the membrane surface. Likewise, Juang and Jiang (1994), Sun *et al.* (1998), and Kocherginsky *et al.* (2003) showed that hydrophilic ultrafiltration membranes, composed of regenerated cellulose or nitrocellulose, could be used to separate W/O emulsions into the respective phases.

Other factors such as flow and ionic concentrations can be used to manipulate separation efficiencies. Thus, hydrodynamic forces have been cited as being important in the coalescence of oil droplets as they pass through various packed beds (Mathavan and Viraraghavan 1992; Lee and Han 1993; Briscoe *et al.* 2000; Cambiella *et al.* 2006). Cambiella *et al.* (2006) observed that droplet coalescence and collection were greatly assisted if salt was added to the mixture, helping to coagulate the oil. Dimov *et al.* (2000) found that oil droplets could be deposited even onto a hydrophilic substrate through the squeezing action of a receding meniscus. Varghese and Cleveland (2008) reported more effective oil removal in the case of larger oil drops, with finer kenaf particles, with higher filtration pressure, with lower pH, and with the presence of a cationic surfactant.

Lim and Huang (2006, 2007a,b) noted that the hydrophobic surface of kapok fibers will allow oil to permeate, but not water. No capillary rise was observed for water on the packed kapok fibers, whereas diesel fuel was able to migrate 20 cm up the material by means of capillary action.

Deployment of Sorbents to Float at the Water Surface

Because most oils have densities lower than that of water, treatment options involving floating sorbents are of great interest. The subsections that follow will consider options including the loose scattering of sorbent material at the water surface (*e.g.* on the top of a layer of spilled oil), absorbent booms, as well as options dependent on wave action or tidal effects.

Self-floating, loose biosorbent materials

When loose sorbent material is spread on the surface of floating oil, the operation can be judged as a success only if the process renders the oil easier to collect. In other words, the goal of such treatment is to convert the spilled oil from a hard-to-manage liquid form into a more manageable solid-bound form. It is also important that the release of the sorbent material to the environment does not in itself contribute to significant environmental harm, especially if some of it fails to be collected after its deployment and use. For instance, if the use of sorbent causes some or all of the oil to sink, then the collection of both the oil and the sorbent may become more difficult (Pushkarev *et al.* 1980). Also, if the sorbent material lacks biodegradability, then it may persist for a long time on a beach, in an estuary, on an ocean floor, or in other environmentally sensitive locations (Ott 2005; Penela-Arenaz *et al.* 2009; DeLaune and Wright 2011). In addition, the sorbent material should not be added in such quantity or form that it interferes with other collection efforts, such as skimming (Fingas 2011a). Finally, most of the oiled sorbent (some would say all of it) should be able to be removed at the end of the operation.

Likely options for spreading of loose sorbent material on top of floating oil include blowing from a boat, or blowing from the shore. It has been proposed that such operations make best sense in removing the last vestiges of oil, *i.e.* as a “polishing” operation after such operations as skimming have been used to remove any relatively thick layers of floating oil (Ghaly and Pike 2001). In any case, the sorption capacity needs to be sufficient for the situation (Cojocaru *et al.* 2011).

Floating structures

Rethmeier and Jonas (2003) describe the use of a floating mat as a means of sorbing spilled oil. A potential advantage of this approach is that the mat can be treated so as to initiate the process of biodegradation of the oil (see later). At least in theory, a used mat could be squeezed between rollers (Pushkarev *et al.* 1980) or even dry-cleaned so that it could be used multiple times.

Using wave/tidal action to aid collection

Another way to collect floating oil at the surface of water takes advantage of wave and/or tide-induced motions. Such motions can induce flows into and out from the void volume of a suitable sorbent structure placed in a fixed, non-floating position so that the water surface periodically moves up and down relative to it. Rather than relying on just diffusion, one takes advantage of convection as an additional mechanism of transporting droplets of oil to the surface of pores in the interior of the sorbent material. This type of system generally requires a firm attachment between the sorbent structure and the ground beneath. Convective transport also can be expected to contribute to contact between the interior of floating absorbent booms and oil-contaminated water due to tides and waves.

Taking Advantage of Biodegradation at the Spill Site

Biodegradation is a natural process that can be expected to take place, though often to a minor degree, regardless of what other methods are being used to collect spilled oil from a natural environment. This section will consider efforts that have been made to speed up or to direct the course of biodegradation.

Natural biodegradation

As has been described in the literature, certain bacteria have the capability to break down the main components of crude oils (Ghaly and Pyke 2001; van Beilen and Funhoff 2007; Suni *et al.* 2006; Rojo 2009; Kristanti *et al.* 2011; CRRC 2012). Such organisms can be found and collected, for instance, near the sites of oil seepage at the sea floor (Wardlaw *et al.* 2008). Given sufficient time, it can be expected that all but the most recalcitrant compounds of spilled oil will be broken down into other, more readily metabolized forms. Limitations to the rates of decomposition include the limited amounts of dissolved oxygen in the water and the initially low levels expected for oil-decomposing bacteria and the associated enzymes. Simanzhenkov and Idem (2003) noted that one liter of oil will have a biological oxygen demand, necessary for its decomposition, corresponding to the dissolved oxygen typically present in about 40,000 liters of water. Another limitation is the time factor. More complete biodegradation of oil under natural conditions can take years, thus limiting its practical application in many spill situations. This limits the biodegradation of oil at sea.

Innoculation

In theory it would be possible to accelerate the decomposition of spilled oil by distributing sufficiently large amounts of hydrocarbon-degrading enzymes or oil-degrading bacteria on the surface of floating oil (Yakimov *et al.* 1998; Oh *et al.* 2000). Due to such factors as wave action, the applied enzymes or bacteria would tend to be washed away, dispersed, and greatly diluted. To overcome such effects, and in an effort to achieve meaningful improvements in biodegradation, various authors have described the use of enzymes in combination with biosorption (Oh *et al.* 2000; Gertler *et al.* 2009). In principle, the sorbent material provides a means of holding both the oil and the enzymes (or the source bacteria) in close proximity and at relatively high concentration, thus favoring decomposition of the oil.

Though lab-based studies of inoculation have shown some promise in terms of acceleration of breakdown of oils (Oh *et al.* 2000; Gertler *et al.* 2009), the general findings have not been convincing. According to Suni *et al.* (2006), there are already sufficient numbers of various bacteria in the natural environment, and the ability of bacteria to multiply their populations is so rapid that inoculation tends to have little net benefit in the longer term. Again, the time factor is an issue; spill cleanups are carried out in the matter of days and natural biodegradation is often on the order of months.

Studies and patents by Varadaraj and coworkers have considered the relationship between the use of various surfactants ("dispersants") and rates of biodegradation. Varadaraj *et al.* (1995b) showed that the degradation of hydrocarbon in soil was accelerated by the presence of polyoxylene sorbitan mono-ester. Such effects can be promoted by addition of nutrients (Varadaraj and Brons 1998; Prince *et al.* 1999). However, different surfactants appear to affect biodegradation differently (Varadaraj *et al.* 1995b), and more such research is needed.

STRATEGIES TO DEAL WITH OIL-CONTAINING SORBENT

Whereas Table A lists about 76 studies dealing with the sorption of oils onto cellulose-based materials, a much lower number of studies have considered what to do with such sorbent materials after they have been used. The subsections that follow will consider options such as landfilling, regeneration, incineration, composting, anaerobic digestion, and combinations of biosorption with various more conventional approaches to dealing with oil spills.

Landfilling

Placement of oil-contaminated materials in landfills has been considered as one of the most likely options in practice (Carro *et al.* 2008; Yeboah and Burns 2011). Such landfilling takes place despite concerns about leaching (Kriipsalu *et al.* 2005; Orupold *et al.* 2008; Coz *et al.* 2011). As noted earlier, oil can easily drain back out of many commonly used sorbents (Wei *et al.* 2003; Khan *et al.* 2004). Landfilling also can be considered as a waste of land and materials, considering various potential alternatives for reuse of oil-containing materials (Yeboah and Burns 2011). Landfilling usually involves measures to prevent leached oil from entering the environment. Some alternatives to landfilling are described in the subsections that follow.

Regeneration

In principle it would be possible to remove most of the oil and to restore a sorbent material to its initial condition. For instance, the material could be subjected to a drycleaning process, in which oils are essentially extracted with a solvent. However, in addition to the expense involved, there are also serious environmental concerns about the solvents employed (Altmann *et al.* 1995; Delery *et al.* 2008; Gold *et al.* 2008). Thus, drycleaning would be hard to justify as a means to achieve environmental benefits. Rather, it is often regarded as being more practical and cost-effective to just use fresh sorbent material on a single-use basis to clean up oily spills (Fingas 2011a).

A general approach based on squeezing the sorbent can be used if one relaxes the requirement that the sorbent be completely decontaminated. The feasibility of squeezing to release oil from sorbent material has been demonstrated in many studies (Choi *et al.* 1993; Inagaki *et al.* 2002a,b; Silva-Tilak 2002; Sun *et al.* 2002, 2003; Yang *et al.* 2002; Deschamps *et al.* 2003a; Radetic *et al.* 2003; Nduka *et al.* 2008; Husseien *et al.* 2009a,b;

Lin *et al.* 2010; Choi *et al.* 2011; Zhu *et al.* 2011a). Ideally, the squeezing operation would release oil in a relatively concentrated form, leaving little oil in the sorbent and also restoring the sorption capacity close to its initial value. Thus, certain sorbents that resist wetting by water can be regarded as advantageous for use in operations that incorporate repeated partial regeneration by squeezing (Pate 1992; Choi 1996; Sun *et al.* 2002, 2003; Rethmeier and Jonas 2003; Wei *et al.* 2003; Suni 2004; Wang *et al.* 2010; Choi *et al.* 2011).

Loss of capacity

As shown in Table A, various studies have reported losses of sorption capacity ranging from zero to 85% when various sorbent materials have been squeezed to release the sorbed oil during multiple cycles of use (see, for instance, Choi *et al.* 1994). More typically, the observed losses have been between 10 and 30% (Johnson *et al.* 1973; Choi 1996; Inagaki *et al.* 2002a; Radetic *et al.* 2003; Lim and Huang 2007a; Abdullah *et al.* 2010; Lin *et al.* 2010; Zhu *et al.* 2011a). In a study using raw cotton fiber sorbent, Choi *et al.* (1994) found that multiple exposure to malathion (the oily material being collected) resulted in removal of the waxy layer from the fiber, thus reducing its effectiveness.

Questions remain regarding the practical or commercial feasibility of batch-wise regeneration of sorbents after their use. Just because a regeneration operation can be demonstrated at the laboratory scale, that does not mean that the practice will necessarily become used commercially. For instance, it does not seem likely that sorbents that have been used to deal with one environmental disaster are likely to be stored, despite their only partially decontaminated condition, for an unknown future potential usage. Rather, it makes sense for such a sorbent to be only re-used immediately at the scene of an ongoing cleanup effort. One promising scheme is based on the concept of a continuous belt of highly elastic sorbent material (Radetic *et al.* 2003). One end of such a belt could be placed in the contaminated water, where it can come into contact with floating oil. The other end could be attached to a drive mechanism, a squeezing device, and a means for collecting the oil. Thus, it makes sense for highly effective sorbent materials based on cellulose to be considered for future developments in skimmer systems, such as some of those that have been listed in Table 2. It has been stated that sorbent materials qualifying for such operations should have a high ability to resist wetting by water, as well as having a high elastic recovery (Rao *et al.* 2007; Lin *et al.* 2010; Choi *et al.* 2011).

Evaporation Followed by Incineration

Due to the generally high water content of cellulose-based sorbents after they have been used to collect oil, treatment options involving conventional drying and incineration are generally not considered to be cost-effective (Choi 1996; Chouchene *et al.* 2012; Jeguirim *et al.* 2012). In other words, more energy may be expended in the incineration of such materials than can be gained from the combustion. In an effort to get around this problem, Chouchene *et al.* (2010; 2012) proposed a three-step process comprised of (a) sorption of the oil onto low-cost cellulosic material, (b) natural evaporation of the water, and (c) incineration with energy recovery. Air emissions were found to be acceptable, at least in the case of the olive oil wastes considered. Based on the 1 cm thickness of material that the cited authors used in their air-drying procedure, the area required for effective solar drying under Mediterranean conditions can be estimated to be more than 100 m^2 for each ton of saturated sorbent material per drying cycle.

Another way to get around the problem of water evaporation is to use a cheap sorbent material that is so hydrophobic that little water is collected. Ericsson (1985) patented the use of a blend of cellulosic pulp with rosin size and various other materials. The mixture was claimed to have low flammability until its use for the sorption of oil. After such use it could be readily burned. Likon *et al.* (2011) employed a similar strategy based on papermill waste sludge that had been hydrophobized with a silane treatment. Varghese and Cleveland (2008) stated that after kenaf had been used multiple times to absorb oil, it was sufficiently low in water content so that it could be combusted without further drying.

Incineration in most countries is now regulated such that incineration of oil-soaked sorbents is prohibited or could only be carried out under strictly controlled conditions.

Composting and Anaerobic Digestion

A composting operation can be defined as biodegradation carried out in such a way that the metabolic processes result in a pronounced rise in temperature, thus accelerating the biodegradation (Hubbe *et al.* 2010). Studies have demonstrated the effectiveness of composting for the treatment of oil-contaminated materials or soils (Ghaly and Pyke 2001; Suni *et al.* 2006; Kristanti *et al.* 2011). Varadaraj and Savage (1998) showed that the decomposition of hydrocarbons contaminants in soil can be promoted by adding cedar chips along with suitable compounds to achieve a favorable elemental balance of C, N, and P.

Another approach, consistent with oil-degrading micro-organisms at the sea floor (Wardlaw *et al.* 2008), may involve anaerobic digestion of oil-contaminated sorbent under optimized conditions (Alimahmoodi and Mulligan 2011; Ji *et al.* 2011; Mohan *et al.* 2011; Rastegar *et al.* 2011; Scherr *et al.* 2012). Given the potential benefits of such approaches, considerably more research will be needed in the future to more fully understand the processes, including the quantification of decomposition rates and the identification of chemical breakdown products.

Extraction to Recover Fuel Value of the Oil

Few researchers have considered the possibility of recovering oils from sorbent materials by chemical means. The intermittent and variable nature of oil spill collection operations tend to discourage interest in such approaches, even if technically feasible. Some research, however, has been carried out in an analogous situation; research has shown that it is feasible to recover oil from waste drilling fluid (Zhu *et al.* 2011b). In the cited study, oil recovery was found to be greatly enhanced by the use of a nonionic surfactant (demulsifier) with either calcium chloride or aluminum sulfate (coagulant), followed by nonionic or cationic acrylamide polymer (flocculant). Another advantage of such recovery of the oil was a less hazardness nature of the residual sludge.

Combining Biosorption with Conventional Technologies

There is potential for cellulose-based sorbents to be used in combination with other well-known measures of dealing with oil spills. The presumption here is that certain remedial measures are more commonly used than those involving the use of sorbents. It is visualized that increased usage of sorption technologies will likely follow if sorbent use is regarded as a way to enhance the results of those other operations.

Skimming

When a layer of oil on water is relatively thick and the water surface is relatively calm, then a mechanical device can be used to collect a layer of fluid, with the aim of capturing essentially all of the floating oil and a minimum of the underlying water (Fingas 2012a).

But conditions are not always ideal for the use of a skimmer, and time may pass before the necessary equipment is in place. Waves at sea often exceed 1 m in height, which can be considered as an approximate limit for the efficient use of skimming equipment. For example, Iglesias and Carballo (2010) reported that wave heights of 1.5 to 4 m were most typical over 44 years of observation in the Bay of Biscay. What then can be done to help hold the oil at the surface of the water, limiting its tendency to spread and weather? Presumably, if the oil becomes sorbed into the pore structure of cellulosic material, then the likelihood and extent of spreading or emulsion formation will be reduced.

Collection of oil onto the surfaces of typical cellulosic materials may not prevent the oil from sinking. Only certain cellulose-based materials have been shown to dependably continue to float on water for long periods in the form of loose particles or fibers (Pate 1992; Deschamps *et al.* 2003a; Korhonen *et al.* 2011; Likon *et al.* 2011; Moura and Lago 2011). Sinkage can become more likely in the course of saturation of the sorbent materials with oil (Lee *et al.* 2007). In addition, excessive quantities of sorbent are expected to interfere with skimmer operations (Fingas 2012a). Al-Marzouqi *et al.* (2003) showed the feasibility of a novel system in which superabsorbent foam was incorporated into a continuous skimming device; a low-density polyurethane sponge material was judged to have the best performance. What might be helpful at this point would be studies of different candidate materials, such as milkweed seed hairs, raw cotton, or kapok – all of which could be grown, harvested, and stored until needed – and an evaluation of their effectiveness under realistic conditions of oil spillage, weather, and skimming operations.

Application of sorbent within oil-containment booms

Floating booms that are most often used to limit the spreading of spilled oil do not have the ability to absorb oil. Sorbent materials might be used in two ways to enhance the effectiveness of such operations. On the one hand, sorbent material could be spread loosely within the circumference of a boom, thus helping to maintain the oil in a more stable form. Indeed, many studies have demonstrated the effectiveness of loose particles or fibers placed directly onto layers of spilled oil (Johnson *et al.* 1973; Browers 1982; Choi *et al.* 1994; Silva-Tilak 2002; Radetic *et al.* 2003; Lim and Huang 2007a; Rajakovic *et al.* 2007).

Sorbent booms

A second way in which sorbent materials can be paired with boom technology is to use engineered products containing pores to imbibe and hold fluid by capillary force. Booms could themselves be constructed using such materials. Current practice is to use sorbent booms, with loose material packaged in a permeable fabric, to line conventional booms. This practice can prevent the loss of light oils under or over the boom. This method will be described more fully in a following section. The assumption is being made here that the solid nature of the used sorbent particles, now containing the oil, is likely to be preferable to the viscous water-in-oil emulsion that might form as a consequence of wave action and weathering. Tests need to be carried out to ascertain whether or not the used sorbent material is easier to handle than the weathered oil itself.

Absorbent booms are available in various forms (Bestvalsup 2012; Spill-kit 2012; Supplylinedirect 2012). Many boom-like sorbent products are not designed to float; thus there is a continuing need to discover or develop inexpensive, ecologically-friendly floatable materials that can be used either as a component, or possibly as the sole filler in a sock-like boom structure. Absorbent socks also can be used in such applications as controlling the run-off from localized spills on land.

Absorbent products also can be prepared in the form of pads, which have a wide variety of possible uses (Browers 1982; Gupta 1988; Correa *et al.* 1997; Chatterjee and Gupta 2002). For instance, Browers (1982) suggested the use of absorbent pads on beaches and on rough terrain. Chatterjee and Gupta (2002) showed that the capacity of sorbent pads could be enhanced by employing nonwoven fabric technologies designed to impart high bulk that renders the pad stable under conditions of use. Bulk can be further enhanced by use of fibers having novel geometries, *e.g.* trilobal cross-section, in the fabric. Needling of a nonwoven structure can be used effectively to provide channels for oil to flow into a fabric and to impart stable bulk and resistance to collapse (Gupta 1988; Pate 1992). In such structures the oil is likely to be held mainly in pores between the fibers, rather than within the interior of the fibers. As discussed earlier, both the pore volume, which determines the absorbent capacity, and the pore size, which determines the rate of absorption, can be engineered as desired by appropriate selection of fiber material parameters and construction technology (Zahid *et al.* 1972; Gupta 1988, 1995; Chatterjee and Gupta 2002).

Combining sorption with enhanced decomposition

It has been shown that bacteria can be immobilized in sorbent materials and thereby used to decompose oil (Oh *et al.* 2000; Suni *et al.* 2006), as also suggested by Rethmeier and Jonas (2003). Efforts to combine sorbent use with enhanced biodegradation face a number of constraints and challenges. Among the most severe constraints is the relatively short period of viability of either bacteria or of enzymes that could be used to inoculate the system. Since bacterial cells can divide and double their population within tens of minutes (Zaritsky *et al.* 2011), depending on such factors as temperature, it is difficult to justify inoculating sorbent material prior to its usage. Also, if the bacteria are not bound to the sorbent, then they may become dispersed in the water phase (Gertler *et al.* 2009).

Suni *et al.* (2006) showed that inoculation with oil-decomposing bacteria had a positive impact only in a nutrient-poor system at short contact times; in more general treatments, where long periods were involved for build-up of populations of bacteria, already present at low levels in the environment, no advantage was found in inoculating the system. In related work Suni *et al.* (2007) found that whereas inoculation had a positive effect in a laboratory setting, there was no advantage of using innoculants in a sea environment; just a few days were sufficient for suitable bacteria of local origin to reach high population densities.

Enzymes can have much greater shelf-life than the bacteria that give rise to them, especially if the enzymes are in a stabilized form (O’Fagain 2003). Thus it is possible to consider treating the sorbent material with enzymes just before it is deployed. However, since the enzymes have no way to reproduce themselves, the net effect of the treatment is likely to be small and localized.

Incorporation of bacteria-supporting nutrients into an oil-sorbent product is likely to be a more promising approach (Ghaly and Pyke 2001; Gertler *et al.* 2009; Kristanti *et al.* 2011). Saez-Navarrete *et al.* (2008) demonstrated that the biomass itself can be considered a nutrient, insofar as it helps to support a viable bacterial community, for which it can serve as an energy source. As noted elsewhere in this article, further research is needed to test the feasibility of nutrient usage in practice and to further refine strategies incorporating renewable materials and natural processes into systems for dealing with the spillage of oil.

CONCLUDING REMARKS

As has been shown by studies cited in this article, substantial progress has been achieved not only in understanding how cellulosic materials can be used to help collect spilled oil, but also in practical demonstrations of how this approach can be used to mitigate effects of oil spills. The effectiveness of biosorption clearly depends not only on the nature of the absorbent material, and the characteristics of the structure or assembly, if any, containing it, but also on the properties of the oil and the presence and characteristics of an aqueous phase. Though a wide range of cellulosic materials have been shown to be effective, the results reviewed in the present article show many advantages to be expected when using either naturally hydrophobic cellulosic sorbents or cellulosic materials that have been rendered more hydrophobic by chemical derivatization.

Significant gaps in knowledge remain regarding what to do with oil-containing cellulosic sorbent material after the biosorption step has been completed. For instance, there is an urgent need for research related to the anaerobic digestion or composting of cellulosic sorbent material that has been used in the collection of crude petroleum. Parallel work needs to consider the most likely alternative schemes, such as landfilling, incineration, and regeneration. The relative environmental effects of different schemes need to be systematically examined, using life cycle analysis.

Investigators who are looking for urgently important but also theoretically challenging projects should be encouraged to consider the field of bioremediation. In the view of the authors, some topics that stand out for research attention include better characterization of phase interactions when oil spreads onto (dry or wet) cellulosic surfaces, mechanisms and factors affecting biodegradation in the presence of sorbent material, and the effects of biosorption on residual toxicity in the environment.

There is also a need for studies focused on the logistical and practical aspects of biosorption, including the advisability and effectiveness of passing contaminated water through a bed of absorbent material, of deploying the sorbent material in booms, and of spreading loose cellulosic material onto floating oil. Also there is a need for studies in which biosorption is employed in combination with other existing measures for dealing with oil spills, such as the use of containment booms and skimmers.

REFERENCES CITED

Abdullah, M. A., Rahmah, A. U., and Man, Z. (2010). "Physicochemical and sorption characteristics of Malaysian *Ceiba pentandra* (L.) Gaertn. as a natural oil sorbent," *J. Hazard Mater.* 177(1-3), 683-691.

Adamson, A. W., and Gast, A. P. (1997). *Physical Chemistry of Surfaces*, 6th Ed., Wiley, New York.

Adebajo, M. O., and Frost, R. L. (2004). "Acetylation of raw cotton for oil spill cleanup application: An FTIR and C-13 MAS NMR spectroscopic investigation," *Spectrochim. Acta Part A – Molec. Biomolec. Spectrosc.* 60(10), 2315-2312.

Adebajo, M. O., Frost, R. L., Kloropogge, J. T., Carmody, S., and Kokot, S. (2003). "Porous materials for oil spill cleanup: A review of synthesis and absorbing properties," *J. Porous Mater.* 10, 159-170.

Aguilera, F., Mendez, L., Pasaro, E., and Laffon, B. (2010). "Review of the effects of exposure to spilled oils on human health," *J. Appl. Toxicol.* 30(4), 291-301.

Ahmad, A. L., Samathi, S., and Hameed, B. H. (2005a). "Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan," *Water Res.* 39, 2483-2494.

Ahmad, A. L., Sumathi, S., and Hameed, B. H. (2005b). "Residual oil and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon: A comparative study," *Chem. Eng. J.* 108, 179-185.

Aisien, F. A., Hymore, F. K., and Ebewele, R. O. (2006). "Comparative absorption of crude oil from fresh and marine water using recycled rubber," *J. Environ. Eng. – ASCE* 132(9), 1078-1081.

Aksu, Z. (2005). "Application of biosorption for the removal of organic pollutants: A review," *Process Biochem.* 40, 997-1026.

Aldhous, P., and Hetch, J. (2010). "Beware long-term damage when cleaning up oil spills," *The New Scientist* 206(2765): 10, DOI:10.1016/S0262-4079(10)61464-9.

Alimahmoodi, M., and Mulligan, C. N. (2011). "Optimization of the anaerobic treatment of a waste stream from an enhanced oil recovery process," *Bioresour. Technol.* 102(2), 690-696.

Al-Marzouqi, A. H., Busamra, A., Mohammed, F., Al-Shehhi, S., and Abdulwahab, W. (2003). "A novel absorbent-skimmer technology for cleaning oil spills," In: Brebbia, C. A., Almorza, D., and LopezAguayo, F. (eds.), *Coastal Engineering VI: Computer Modelling and Experimental Measurements of Seas and Coastal Regions*, Environmental Studies Series, Vol. 9, pp. 205-214.

Altmann, L., Neuhann, H. F., Kramer, U., Witten, J., and Jermann, E. (1995). "Neurobehavioral and neurophysiological outcome of chronic low-level tetrachloroethene exposure measured in neighborhoods of dry cleaning shops," *Environ. Res.* 69(2), 83-89.

Annuciado, T. R., Sydenstricker, T. H. D., and Amico, S. C. (2005). "Experimental investigation of various vegetable fibers as sorbent materials for oil spill," *Mar. Pollut. Bull* 50, 1340-1346.

ASTM (2012). *Standard Test Method for Sorbent Performance of Adsorbents*, American Society for Testing and Materials, Conshohocken, PA.

Atlas, R., and Hazen, T. C. (2011). "Oil biodegradation and bioremediation: A tale of the two worst spills in U.S. history," *Environmental Science & Technology* 45(16), 6709-6715.

Aulin, C., Shchukarev, A., Lindqvist, J., Malmström, E., Wågberg, L., and Lindström, T. (2008). "Wetting kinetics of oil mixtures on fluorinated model cellulose surfaces," *J. Colloid Interface Sci.* 317(2), 556-567.

Aurell, J., and Gullett, B. K. (2010). "Aerostat sampling of PCDD/PCDF emissions from the Gulf oil spill in situ burns," *Environmental Science and Technology* 44(24), 9431-9437.

Ball, J. F. (1973). "Method of making a hydrophobic fibrous product," *US Pat.* 3,770,575.

Baltazar-y-Jimenez, A., and Bismarck, A. (2007). "Surface modification of lignocellulosic fibres in atmospheric air pressure plasma," *Green Chem.* 9(10), 1057-1066.

Bayat, A., Aghamiri, S. F., Moheb, A., and Vakili-Nezhaad, G. R. (2005). "Oil spill cleanup from sea water by sorbent materials," *Chem Eng. Technol.* 28(12), 1525-1528.

Bayer, I. S., Fragouli, D., Attanasio, A., Sorce, B., Bertoni, G., Brescia, R., Di Corato, R., Pellegrino, T., Kalyva, M., Sabella, S., Pompa, P. P., Cingolani, R., and Athanassiou, A. (2011). "Water-repellent cellulose fiber networks with multifunctional properties," *ACS Appl. Mater. Interfac.* 3(10), 4024-4031.

Berninger, J. P., Williams, E. S., and Brooks, B. W. (2011). "An initial probabilistic hazard assessment of oil dispersants approved by the United States National Contingency Plan," *Environ. Toxic. Chem.* 30(7), 1704-1708.

Bestvalsup (2012). "Absorbent pads, spill kits, absorbent socks, booms," http://www.bestvalsup.com/.

Biermann, O., Hadicke, E., Koltzenburg, S., and Muller-Plathe, F. (2001). "Hydrophilicity and lipophilicity of cellulose crystal surfaces," *Angew. Chemie-Intl. Ed.* 40(20), 3822-3825.

Bobra, M. (1992). "Solubility behaviour of petroleum oils in water," Environment Canada, Environmental Protection Directorate, River Road Environmental Technology Centre, Ottawa, ON, Report series (River Road Environmental Technology Centre) ; EE-130. TD171.5.C2 R476 no.130. Online access: http://www.boemre.gov/tarprojects/120/120AX.PDF

Bobra, M., Fingas, M., and Tennyson, E. (1992). "When oil spills emulsify," *CHEMTECH* 22, 236-241.

Bolto, B., and Gregory, J. (2007). "Organic polyelectrolytes in water treatment," *Water Res.* 41(11), 2301-2324.

Briscoe, B. J., Luckham, P. F., Jayarajah, J. N., and Akeju, T. (2000). "Separation of emulsions using fibrous fabric," *Colloids Surf. A – Physicochem. Eng. Aspects* 163(2-3), 151-164.

Browers, S. D. (1982). "Understanding sorbents for cleaning up spills," *Plant Eng.* 3, 219-221.

Brugnara, M., Della Volpe, C., Maniglio, D., Siboni, S., Negri, M., and Gaeti, N. (2006). "Wettability of porous materials. I: The use of Wilhelmy experiment: The cases of stone, wood and non-woven fabric," In: Mittal, K. L. (ed.), *Contact Angle, Wettability and Adhesion*, VSP - an imprint of BRILL, Vol. 4, pp. 115-141.

Brunauer, S., Emmett, P. H., and Teller, E. (1938). "Adsorption of gases in multimolecular layers," *J. Amer. Chem. Soc.* 60, 309-319.

Buckley, J. S. (1998). "Wetting alteration of solid surfaces by crude oils and their asphaltenes," *Revue Inst. Fracais Petrole* 53(3), 303-312.

Buckley, J. S., and Wang, J. X. (2002). "Crude oil and asphaltene characterization for prediction of wetting alteration," *J. Petroleum Sci. Eng.* 33(1-3), 195-202.

Burton, N. H. K., Musgrove, A. J., Rehfisch, M. M., and Cark, N. A. (2010). "Birds of the Severn Estuary and Bristol Channel: Their current status and key environmental issues," *Marine Pollut. Bull*. 61, 115-123.

Cambiella, A., Ortea, E., Rios, G., Benito, J. M., Pazos, C., and Coca, J. (2006). "Treatment of oil-water emulsions: Performance of a sawdust bed filter," *J. Hazard Mater.* 131, 195-199.

Carmody, O., Frost, R., Xi, Y. F., and Kokot, S. (2007). "Surface characterisation of selected sorbent materials for common hydrocarbon fuels," *Surface Sci.* 601(9), 2066-2076.

Carmody, O., Frost, R., Xi, Y., and Kokot, S. (2008). "Selected adsorbent materials for oil-spill cleanup - A thermoanalytical study," *J. Thermal Anal. Calorim.* 91(3), 809-816.

Carrillo, C. A., Saloni, D., Lucia, L. A., Hubbe, M. A., and Rojas, O. J. (2012). "Capillary flooding of wood with microemulsions from Winsor I systems," *J. Colloid Interface Sci.* 381(1), 171-179.

Carro, D., Delgado, J., Vazquez, A., Barrientos, V., and Juncosa, R. (2008). "Final disposal of the wastes associated with the oil spill of the tanker prestige through its stabilization with quicklime and granite fines," *Soil Sediment Contam.* 17(4), 393-410.

Cassie, A. B. D., and Baxter, S. (1944). "Wettability of porous surfaces," *Trans. Faraday Soc.* 40, 546-551.

Cervin, N. T., Aulin, C., Larsson, P. T., and Wågberg, L. (2012). "Ultra porous nanocellulose aerogels as separation medium for mixtures of oil/water liquids," *Cellulose* 19(2), 401-410.

Chapman, H., Purnell, K., Law, R. J., and Kirby, M. F. (2007). "The use of chemical dispersants to combat oil spills at sea: A review of practice and research needs in Europe," *Marine Pollut. Bull*. 54(7), 827-838.

Chatterjee, P. K., and Gupta, B. S. (eds.) (2002). *Absorbent Technology,* Vol. 13 of *Textile Science and Technology* series, Elsevier, Amsterdam.

Choi, H. M. (1996). "Needlepunched cotton nonwovens and other natural fibers as oil cleanup sorbents," *J. Environ. Sci. Heath. Pt. A – Environ. Sci. Eng. Toxic Hazard Subst. Control* 31(6), 1441-1457.

Choi, H.-M., and Cloud, R. M. (1992). "Natural sorbents in oil spill cleanup," *Environ. Sci. Technol.* 26(4), 772-776.

Choi, H.-M., Kwon, H.-J., and Moreau, J. P. (1993). "Cotton nonwovens as oil spill cleanup sorbents," *Textile Res. J.* 63, 211-218.

Choi, H., Moreau, J. P., and Srinivasan, M. (1994). "Cleanup of agrochemical spills using cotton sorbents," *J. Environ. Sci. Health. Part A – Environ. Sci. Eng. Toxic Hazard. Subt. Control.* 29(10), 2151-2168.

Choi, S.-J., Kwon, T.-H., Im, H., Moon, D.-I., Baek, D. J., Seol, M.-L., Duarte, J. P., and Choi, Y.-K. (2011). "A polydimethylsiloxane (PDMS) sponge for the selective absorption of oil from water," *ACS Appl Mater. Interfaces* 3(12), 4552-4556.

Choi, S. T., and Huber, D. J. (2009). "Differential sorption of 1-methylcyclopropene to fruit and vegetable tissues, storage and cell wall polysaccharides, oils, and lignins," *Postharvest Biology Technol.* 52, 62-70.

Chouchene, A., Jeguirim, M., Favre-Reguillon, A., Trouve, G., Le Buzit, G., Khiari, B., and Zagrouba, F. (2012). "Energetic valorisation of olive mill wastewater impregnated on low cost absorbent: Sawdust versus olive solid waste," *Energy* 39(1), 74-81.

Chouchene, A., Jeguirim, M., Trouve, G., Favre-Reguillon, A., and Le Buzit, G. (2010). "Combined process for the treatment of olive oil mill wastewater: Absorption on sawdust and combustion of the impregnated sawdust," *Bioresour. Technol.* 101(18), 6962-6971.

Claesson, P. M., Kjellin, M., Rojas, O. J., and Stubenrauch, C. (2006). "Short-range interactions between non-ionic surfactant layers," *Physical Chemistry Chemical Physics* 8(47), 5501-5514.

Clayton, J. R., Jr., Payne, J. R., and Farlow, J. S. (1993). *Oil Spill Dispersants: Mechanisms of Action and Laboratory Tests,* C. K. Smoley, CRC Press, Boca Raton, FL, USA.

Cojocaru, C., Macoveanu, M., and Cretescu, I. (2011). "Peat-based sorbents for the removal of oil spills from water surface: Application of artificial neural network modeling," *Colloids Surf. A – Physicochem. Eng. Aspects* 384(1-3), 675-684.

Correa, M., Padron, E., and Petkoff, I. (1997). "The San Rafael de Laya oil spill: A case of cleanup and remediation in Venezuela," *1997 Intl. Oil Spill Conf.: Improving Environ. Protec.*, Ft. Lauderdate, FL, April 7-10, 932-935.

Coz, A., Villegas, M., Andres, A., Viguri, J. R., Mantzavinos, D., and Xekoukoulotakis, N. P. (2011). "Management scenarios for olive oil mill waste based on characterization and leaching tests," *J. Chem. Technol. Biotech.* 86(12), 1542-1547.

CRRC (2012). "The future of dispersant use in oil spill response initiative," Report from the Coastal Response Research Center, Research Planning Incorporated, National Oceanic and Atmospheric Administration (NOAA), downloaded March 2013; http://www.crrc.unh.edu/workshops/dispersant_future_11/Dispersant_Initiative_FINALREPORT.pdf

Cumo, F., Gugliermetti, F., and Guidi, G. (2007). "Best available techniques for oil spill containment and clean-up in the Mediterranean Sea," *Water Resources Management IV, WIT Trans. Ecology Environ*. 103, 527-535.

Curbelo, F. D. S., Garnica, A. I. C., Oliveira, E. L., and Neto, E. L. B. (2006). "Oil removal in produced water by adsorption using expanded and hydrophobized vermiculite as adsorbent," *Afinidad* 62(521), 35-39.

Daiminger, U., Nitsch, W., Plucinski, P., and Hoffmann, S. (1995). "Novel techniques for oil-water separation," *J. Membrane Sci.* 99, 197-203

Dankovich, T. A., and Hsieh, Y.-L. (2007). "Surface modification of cellulose with plant triglycerides for hydrophobicity," *Cellulose* 14(5), 469-480.

Dave, D., and Ghaly, A. E. (2011). "Remediation technologies for marine oil spills: A critical review and comparative analysis," *Amer. J. Environ. Sci.* 7(5), 424-440.

DeLaune, R. D., and Wright, A. L. (2011). "Projected impact of Deepwater Horizon oil spill on US Gulf Coast wetlands," *Soil Sci. Soc. Amer. J.* 75(5), 1602-1612.

Delery, L., Chiappini, L., and Cicolella, A. (2008). "Assessment of population exposure to tetrachloroethylene emissions from French dry-cleaning facilities and their associated health risks," *Environ. Risq. Sante* 7(5), 331-340.

Denesuk, M., Zelinski, B. J. J., Kreidl, N. J., and Uhlmann, D. R (1994). "Dynamics of incomplete wetting on porous materials," *J. Colloid Interface Sci.* 168(1), 142-151.

DePetris, R. (1993). "Oil sorbent products and method of making same," *US Pat.* 5,186,831.

Deschamps, G., Caruel, H., Borredon, M. E., Albasi, C., Riba, J. P., Bonnin, C., and Vignoles, C. (2003b). "Oil removal from water by sorption of hydrophobic cotton fibers. 2. Study of sorption properties in dynamic mode," *Environ. Sci. Technol.* 3721), 5034-5039.

Deschamps, G., Caruel, G., Borredon, M. E., Bonnin, C., and Vignoes, C. (2003a). "Oil removal from water by selective sopriton on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents," *Environ. Sci. Technol.* 37, 1013-1015.

Diersch, H. J. G., Clausnitzer, V., Myrnyy, V., Rosati, R., Schmidt, M., Beruda, H., Ehrnsperger, B. J., and Virgilio, R. (2010). "Modeling unsaturated flow in absorbent swelling porous media: Part 1. Theory," *Transport in Porous Media* 83(3), 437-464.

Dill, K. A., Truskett, T. M., Vlachy, V., and Hribar-Lee, B. (2005). "Modeling water, the hydrophobic effect, and ion solvation," *Ann. Rev. Biophys. Biomol. Struc.* (Ser.: *Ann. Rev. Biophys.*) 34, 173-199.

Dimov, N. K., Ahmed, E. H., Alargova, R. G., Kralchevsky, P. A., Durbut, P., Broze, G., and Mehreteab, A. (2000). "Deposition of oil drops on a glass substrate in relation to the process of washing," *J. Colloid Interface Sci.* 224(1), 116-125.

Ding, L., Li, Y., Jia, D., Deng, J. P., and Yang, W. T. (2011). "Beta-cyclodextrin-based oil-absorbents: Preparation, high oil absorbency and reusability," *Carbohydrate Polymers* 83(4), 1990-1996.

Djikaev, Y. S., and Ruckenstein, E. (2011). "The variation of the number of hydrogen bonds per water molecule in the vicinity of a hydrophobic surface and its effect on hydrophobic interactions," *Curr. Opin. Colloid Interface Sci.* 16(4), 272-284.

Drummond, C., and Israelachvili, J. (2004). "Fundamental studies of crude oil-surface water interactions and its relationship to reservoir wettability," *J. Petroleum Sci. Eng.* 45(1-2), 61-81.

Dubey, M. K., Pang, S. S., and Walker, J. (2012). "Oil uptake by wood during heat-treatment and post-treatment cooling, and effects on wood dimensional stability," *Eur. J. Wood Wood Prods.* 70(1-3), 183-190.

Ena, A., Pintucci, C., Faraloni, C., and Torzillo, G. (2009). "An eco-compatible process for the depuration of wastewater from olive mill industry," *Water Sci. Technol.* 60(4), 1055-1063.

Ericsson, T., Gylfe, S., and Hedblom, M. O. (1985). "Process for the absorption of organic liquids by use of a hydrophobic fibrous material," *US Pat.* 4,519,918.

Ericsson, T. (1985). "Particulate oil-absorbing composition to absorb oil," *US Pat.* 4,537,877.

Eriksson, M., Notley, S. M., and Wågberg, L. (2007). "Cellulose thin films: Degree of cellulose ordering and its influence on adhesion," *Biomacromol.* 8(3), 912-919.

Evans, D. D., Mulholland, G. W., Baum, H. R., Walton, W. D., and McGrattan, K. B. (2001). "In situ burning of oil spills," *J. Res. Nat. Inst. Standards Technol.* 106(1), 231-278.

Faghihnejad, A., and Zeng, H. (2012). "Hydrophobic interactions between polymer surfaces: Using polystyrene as a model system," *Soft Matter* 8, 2746-2759.

Fazal, R. A., and Milgram, J. H. (1979). "The effects of surface phenomena on the spreading of oil on water," Massachusetts Inst. Technol., Report No. MITSG 79-31.

Fingas, M. (2012a). *The Basics of Oil Spill Cleanup*, Third Edition, Lewis Publ., Boca Raton, FL, USA.

Fingas, M. (2011a). *Oil Spill Science and Technology*, Elsevier, Amsterdam.

Fingas, M. (2011b). "In-situ burning," Chapter 23, in: *Oil Spill Science and Technology*, M. Fingas (ed.), Gulf Publishing Company, New York, NY, pp. 737-903.

Fingas, M. (2012b). "Introduction to oil chemistry and properties," In: *Proceedings of the Thirty-fifth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 951-980.

Fingas, M. (2012c). "Vegetable oil spills: Oil properties and behavior," In: *Proceedings of the Thirty-fifth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 884-902.

Fingas, M., and Fieldhouse, B. (2011). "Review of solidifiers," In: *Oil Spill Science and Technology*, Fingas, M. (ed.), Gulf Publishing Co., New York, Ch. 22, pp. 713-733.

Fowkes, F. M. (1964). *Contact Angle, Wettability and Adhesion*, American Chemical Society, Washington, DC.

Fox, H. W., Hare, E. F., and Zisman, W. A. (1955). "Wetting properties of organic liquids on high energy surfaces," *J. Phys. Chem.* 59(10), 1097-1106.

Fox, H. W., and Zisman, W. A. (1952). "The spreading of liquids on low energy surfaces. 1. Polytetrafluoroethylene," *J. Colloid Interface Sci.* 5(6), 514-531.

Fröberg, J. C., Rojas, O. J., and Claesson, P. M. (1999). "Surface forces and measuring techniques," *International Journal of Mineral Processing* 56, 1-30

Frontera, A., Quinonero, D., and Deya, P. M. (2011). "Cation-pi and anion-pi interactions," *Wiley Interdisciplinary Reviews – Computational Molecular Science* 1(3), 440-459.

Fuller, H. I. (1971). "Use of floating absorbents and gelling techniques for combating oil spills on water," *J. Inst. Petrol.* 57(553), 35-43.

Furutaka, S., Kondo, H., and Ikawa, S. (2001). "Infrared spectroscopic study of water-aromatic hydrocarbon mixtures at high temperatures and pressures," *Bull. Chem. Soc. Japan* 74(10), 1775-1788.

Gane, P. A. C. (2004). "Absorption properties of coatings: A selected overview of absorption criteria derived from recent pore network modelling," *J. Dispersion Sci. Technol.* 25(4), 389-408.

Gao, Y., Bai, L., Zhou, Y. T., Zhang, L. P., and Li, F. X. (2011). "Availability of chemically modified wheat straw application on oil spill clean up," In: Cao, Z., He, Y. H., Sun, L., and Cao, X. Q. (eds.), *Application of Chemical Engineering*, Pts. 1-3, Book Series: Advanced Materials Research Vol. 236-238, 301-304.

Gao, Y. A., Zhang, X. L., Qu, P., Zhang, L. P., and Li, S. A. (2010). "Synthesis and oil absorption of chemical modified wood waste materials," In: Li, J. H., and Hu, H. L. (eds.), Selected Proceedings of the Fifth International Conference on Waste Management and Technology (ICWMT 5), 244-247.

Gao, Y., Zhou, Y. T., Zhang, X. L., Zhang, L. P., and Qu, P. (2012). "Synthesis and characteristics of graft copolymers of poly(butyl acrylate) and cellulose fiber with ultrasonic processing as a material for oil absorption," *BioResources* 7(1), 135-147.

Gertler, C., Gerdts, G., Timmis, K. N., and Golyshin, P. N. (2009). "Microbial consortia in mesocosm bioremediation trial using oil sorbents, slow-release fertilizer and bioaugmentation," *FEMS Microbiol. Ecol.* 69(2), 288-300.

Ghaly, A. E., and Pyke, J. B. (2001). "In-vessel bioremediation of oil-contaminated peat," *Energy Sources* 23(4), 305-325.

Ghannam, M. T., (2003). "Spreading behavior of crude oil over limestone substrate," *J. Colloid Interface Sci.* 262(2), 435-441.

Good, R. J., Shu, L. K., Chiu, H. C., and Yeung, C. K. (1996). "Hydrogen bonding and the interfacial component of adhesion: Acid/base interactions of corona-treated polypropylene," *J. Adhesion* 59(1-4), 25-37.

Gold, L. S., De Roos, A. J., Waters, M., and Stewart, P. (2008). "Systematic literature review of uses and levels of occupational exposure to tetrachloroethylene," *J. Occup. Environ. Hyg.* 5(12), 807-839.

Gouin, H. (2001). "The wetting problem of fluids on solid surfaces: Dynamics of lines and contact angle hysteresis," *J. Physique IV* 11(PR6), 261-268.

Gouin, H. (2003a). "The wetting problem of fluids on solid surfaces. Part 1: The dynamics of contact lines," *Continuum Mechanics Thermodyn.* 15(6), 581-596.

Gouin, H. (2003b). "The wetting problem of fluids on solid surfaces. Part 2: The contact angle hysteresis," *Continuum Mechanics Thermodyn.* 15(6), 597-611.

Graham, P. (2010). "Deep sea oil spill cleanup techniques: Applicability, trade-offs and advantages," Proquest Discovery Guides, 15 pp., http://www.csa.com/discoveryguides/oil/review.pdf , downloaded 2013.

Gruber, E., Großmann, and Schempp, W. (1996). "Interactions of synthetic cationic polymers with fibers and fillers. Part 1. The effect of adsorption," *Wochenbl. Papierfabr.* 124(1), 4-6, 8, 10-11.

Gui, X., Wei, J., Wang, K., Cao, A., Zhu, H., Jia, Y., Shu, Q., and Wu, D. (2010). "Carbon nanotube sponges," *Advanced Materials* 22, 617-621.

Gupta, B. S. (1988). "The effect of structural factors on the absorbent characteristics of nonwovens," *Tappi J.* 71(8), 147-152.

Gupta, B. S., and Hong, C. J. (1995). "Absorbent characteristics of nonwovens containing cellulosic fibers," *INDA, INJ.* 7(1), 34-43.

Hamaker, H. C. (1937). "The London–van der Waals attraction between spherical particles," *Physica* IV, 1058.

Hammer, M. U., Anderson, T. H., Chaimovich, A., Shell, M. S., and Israelachvili, J. (2010). "The search for the hydrophobic force law," *Faraday Disc.* 146, 299-308.

Haussard, M., Gaballah, I., Nanari, N., de Donato, P., Barrès, O., and Villieras, F. (2003). "Separation of hydrocarbons and lipid from water using treated bark," *Water Res.* 37(2), 362-374.

He, J., Ding, L., Deng, J. P., and Yang, W. T. (2012). "Oil-absorbent beads containing beta-cyclodextrin moieties: Preparation via suspension polymerization and high oil absorbency," *Polymers Adv. Technol.* 23(4), 810-816.

Hejazi, V., and Nosonovsky, M. (2012). "Wetting transitions in two-, three-, and four-phase systems," *Langmuir* 28(4), 2173-2180.

Hellmich, J. (2011). "Deepwater horizon oil spill response and cleanup," *EM: Air and Waste Management Association's Magazine for Environmental Managers*, (June), pp. 24-27.

Hiberty, P. C., and Shaik, S. (2005). "Some answers to frequently asked questions about the distortive tendencies of pi-electronic system," *Theor. Chem. Accounts* 114(1-3), 169-181.

Hiemenz, P. C., and Rajagopalan, R. (1997). *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York.

Hlavacek, M. (1995). "Break-up of oil-in-water emulsions induced by permeation through a microfiltration membrane," *J. Membrane Sci.* 102, 1-7.

Hodgson, K. T. (1994). "A review of paper sizing using alkyl ketene dimer versus alkenyl succinic anhydride," *Appita* 47(5), 402-406.

Hong, A. C., Fane, A. G., and Burford, R. P. (2002). "The effects of intermittent permeate flow and crossflow on membrane coalescence of oil-in-water emulsions," *Desalination* 144(1-3), 185-191.

Hori, K., Flavier, M. E., Kuga, S., Lam, T. B. T., and Liyama, K. (2000). "Excellent oil absorbent kapok [*Ceiba pentandra (L.) Gaertn*.] fiber: Fiber structure, chemical characteristics, and application," *J. Wood Sci.* 46(5), 401-404.

Huang, X. F., and Lim, T. T. (2006). "The performance and mechanism of hydrophobic–oleophilic kapok filter for oil/water separation," *Desalination* 190(1-3), 295-307.

Hubbe, M. A., Beck, K. R., O'Neal, G., and Sharma, Y. C. (2012a). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 2. Dyes," *BioResources* 7(2), 2592-2687.

Hubbe, M. A., Hasan, S. H., and Ducoste, J. J. (2011). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals," *BioResources* 6(2), 2161-2287.

Hubbe, M. A., Nazhad, M., and Sánchez, C. (2010). "Composting as a way to convert cellulosic biomass and organic waste into high-value soil amendments: A review," *BioResources* 5(4), 2808-2854.

Hubbe, M. A., Payne, K. C., Jackson, C. D., Aizpurua, C. E., and Rojas, O. J. (2012b). "Application of cellulosic fiber materials for the remediation of petroleum spills in water," Proceedings, 4th Intl. Conf. Pulping, Papermaking and Biotechnol., Nov. 7-9, 2012, Nanjing, China.

Hubbe, M. A., Rojas, O. J., Lucia, L. A., and Jung, T. M. (2007). "Consequences of the nanoporosity of cellulosic fibers on their streaming potential and their interactions with cationic polyelectrolytes," *Cellulose* 14(6), 655-671.

Husseien, M., Amer, A. A., El-Maghraby, A., and Hamedallah, N. (2009a). "A comprehensive characterization of corn stalk and study of carbonized corn stalk in dye and gas oil sorption," *J. Anal. Appl. Pyrolysis* 86(2), 360-363.

Husseien, M., Amer, A. A., El-Maghraby, A., and Taha, N. A. (2009b). "Availability of barley straw application on oil spill clean up," *Intl. J. Environ. Scie. Technol.* 6(1), 123-130.

Hussein, M., Amer, A. A., and Sawsan, I. I. (2009c). "Oil spill sorption using carbonized pith bagasse. Application of carbonized pith bagasse as loose fiber," *Global Nest J.* 11(4), 440-448.

Hutchinson, G. H., and Davison, J. W. (2008). "Some applications of viscometry from studies on the absorption of vegetable oils and solvents by paper substrates," *J. Coatings Technol. Res.* 5(3), 365-376, 377.

Ibrahim, S., Ang, H.-M., and Wang, S. (2009). "Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw," *Bioresour. Technol.* 100, 5744-5749.

Iglesias, G., and Carballo, R. (2010). "Wave energy and nearshore hot spots: The case of the SE Bay of Biscay," *Renewable Energy* 35(11), 2490-2500.

Inagaki, M., Kawahara, A., and Konno, H. (2002a). "Sorption and recovery of heavy oils using fir fibers carbonized and their recycling," *Carbon* 40, 105-111.

Inagaki, M., Kawahara, A., Nishi, Y., and Iwashita, N. (2002b). "Heavy oil sorption and recovery by using carbon fiber felts," *Carbon* 40, 1487-1492.

ITOPF (2012). International Tanker Owners Pollution Federation, Response to Marine Oil Spills, 2nd Edition, Whiterby Seamanship, Edinborough, Scotland, 2012

Jacob, P. N., and Berg, J. C. (1993). "Contact angle titrations of pulp fiber furnishes," *Tappi J.* 76(5), 133-137.

Jeguirim, M., Chouchène, A., Réguillon, A. F., Trouvé, G., and Le Buzit, G. (2012). "A new valorisation strategy of olive mill wastewater: Impregnation on sawdust and combustion," *Resources, Conservation and Recycling* 59, 4-8.

Ji, G. D., Tan, Y. F., and Zhang, L. H. (2011). "Bacterial and granular sludge characteristics in an ultrahigh-temperature upflow anaerobic sludge blanket reactor treating super heavy oil-containing wastewater," *Environ. Eng. Sci.* 28(2), 129-137.

Jin, H. X., Dong, B., Wu, B., and Zhou, M. H. (2012). "Oil absorptive polymers: Where is the future?" *Polym.-Plastic Technol. Eng.* 51(2), 154-159.

Johansen, O., Rye, H., and Cooper, C. (2003). "DeepSpill - Field study of a simulated oil and gas blowout in deep water," *Spill Sci. Technol. Bull.* 8(5-6), 433-443.

Johnson, R. E., Jr., and Dettre, R. H. (1969). "Wettability and contact angles," In: *Surface and Colloid Science*, Matijević, E. (ed.), Wiley, New York, Vol. 2, pp. 85-153.

Johnson, R. F., Marjrikar, T. G., and Halligan, J. E. (1973). "Removal of oil from water surfaces by sorption on unstructured fibers," *Environ. Sci. Technol.* 7(5), 439-443.

Juang, R. S., and Jiang, J. D. (1994). "Application of batch ultrafiltration to the separation of w/o emulsion in liquid surfactant membrane process," *J. Membrane Sci.* 96(3), 193-203.

Justino, C. I. L., Pereira, R., Freitas, A. C., Rocha-Santos, T. A. P., Panteleitchouk, T. S. L., and Duarte, A. C. (2012). "Olive oil mill wastewaters before and after treatment: A critical review from the ecotoxicological point of view," *Ecotoxicology* 21(2), 615-629.

Kadla, J. F., and Gilbert, R. D. (2000). "Cellulose structure: A review," *Cellulose Chem. Technol.* 34(3-4), 197-216.

Khan, E., Virojnagud, W., and Ratpukdi, T. (2004). "Use of biomass sorbents for oil removal from gas station runoff," *Chemosphere* 57, 681-689.

Kilpatrick, P. K. (2012). "Water-in-crude oil emulsion stabilization: Review and unanswered questions, "*Energy Fuels* 26(7), 4017-4026.

Knudsen, H. D. (1990). "Milkweed floss fiber for improving nonwoven products," In: TAPPI Nonwovens Conf., TAPPI Press, Atlanta.

Kocherginsky, N. M., Tan, C. L., and Lu, W. F. (2003). "Demulsification of water-in-oil emulsions via filtration through a hydrophilic polymer membrane," *J. Membrane Sci.* 220(102), 117-128.

Kokal, S. (2002). "Crude-oil emulsions: A state-of-the-art review," *SPE Production & Facilities* 20(1), 5-13.

Koltuneiwicz, A. B., and Field, R. W. (1996). "Process factors during removal of oil-in-water emulsions with cross-flow microfiltration," *Desalination* 105, 79-89.

Korhonen, J. T., Kettunen, M., Ras, R. H. A., and Ikkala, O. (2011). "Hydrophobic nanocellulose aerogels as floating, sustainable, reusable, and recyclable oil absorbents," *ACS Appl. Mater. Interfaces* 3(6), 1813-1816.

Kriipsalu, M., Marques, M., and Hogland, W. (2005). "Remediation of an oily leachate pond in Estonia," *Waste Manag. Res.* 23(6), 541-549.

Kristanti, R. A., Hadibarata, T., Toyama, T., Tanaka, Y., and Mori, K. (2011). "Bioremediation of crude oil by white rot fungi polyporus sp S133," *J. Microbiol. Biotechnol.* 21(9), 995-1000.

Kropp, K. G., and Fedorak, P. M. (1998). "A review of the occurrence, toxicity, and biodegradation of condensed thiophenes found in petroleum," *Can. J. Microbiol.* 44(7), 605-622.

Kumagai, S., Noguchi, Y., Kurimoto, Y., and Takeda, K. (2007). "Oil adsorbent produced by the carbonization of rice husks," *Waste Manag.* 27(4), 554-561.

Lee, B. G., Lee, H. J., Shin, D. Y., Jeong, Y. H., Wu, J. C., Cho, D. H., Lee, K. Y, Kim, D. E., Kang, W. S., and Goh, Y. G. (2007). "Effect of grinding and extraction of lignocellulosic fiber on oil sorption," In: Kim, H., Hojo, J., and Lee, S. W. (eds.), *Eco-Materials Processing and Design VIII, Book Series: Materials Science Forum*, Vol. 544-545, pp. 553-556.

Lee, E. C., and Han, K. N. (1993). "The breakage behavior of liquid membrane emulsion in a packed bed," *Hydrometallurgy* 32(2), 233-245.

Lee, J. H., Kim, S. H., and Oh, K. W. (2006). "Image analysis: A novel technique to determine the efficiency of wiping cloths," *Fibers Polymers* 7(1), 73-78.

Li, L., Ding, L. H., Tu, Z. H., Wan, Y. H., Clausse, D., and Lanoiselle, J. L. (2009). "Recovery of linseed oil dispersed within an oil-in-water emulsion using hydrophilic membrane by rotating disk filtration system," *J. Membrane Sci.* 342(1-2), 70-79.

Likon, M., Cernec, F., Svegl, F., Saarela, J., and Zimmie, T. F. (2011). "Papermill industrial waste as a sustainable source for high efficiency absorbent production," *Waste Manag.* 31(6), 1350-1356.

Lim, T.-T., and Huang, X. (2006). "In situ oil/water separation using hydrophobic-oleophilic fibrous wall: A lab-scale feasibility study for groundwater cleanup," *J. Hazardous Mater.* B137, 820-826.

Lim, T. T., and Huang, X. F. (2007a). "Evaluation of kapok (*Ceiba pentandra* (L.) Gaertn.) as a natural hollow hydrophobic-oleophilic fibrous sorbent for oil spill cleanup," *Chemosphere* 66(5), 955-963.

Lim, T. T., and Huang, X. (2007b). "Evaluation of hydrophobicity/oleophilicity of kapok and its performance in oily water filtration: Comparison of raw and solvent-treated fibers," *Industrial Crops Prod.* 26(2), 125-134.

Lin, C., Hong, Y. J., and Hu, A. H. (2010). "Using a composite material containing waste tire powder and polypropylene fiber cut end to recover spilled oil," *Waste Manag.* 30(2), 263-267.

Longo, C., Savaris, M., Zeni, M., Brandalise, R. N., Grisa, A. M. C. (2011). "Degradation study of polypropylene (PP) and bioriented polypropylene (BOPP) in the environment," *Mater. Res. Ibero-Amer. J. Mater.* 14(4), 442-448.

Lu, Q., Oh, D. X., Lee, Y., Jho, Y., Hwang, D. S., and Zeng, H. (2013). "Nanomechanics of cation-π interactions in aqueous solution," *Angewandte Chemie International Edition*, DOI: 10.1002/anie.201210365.

Lucas, R. (1918). "Rate of capillary assension of liquids," *Kolloid Z.* 23, 15-22.

Ludwick, A. G., Aglan, H. A., Abdalla, M. A., Badran, B., Ashour, M., Morcos, V., Hassan, R., and Mahmoud, M. (2003). "Chemical and engineering modification of bagasse for oil absorption," Proceedings of the 2002 National Conference on Environmental Science and Technology," Uzochukwu, G. A., Schimmel, K., Reddy, G. B., Chang, S. Y, and Kabadi, V, (eds.), 313-321.

Mahadevi, A. S., and Sastry, G. N. (2012). "Cation−π interaction: Its role and relevance in chemistry, biology, and material science," *Chem. Rev.* DOI: 10.1021/cr30022d.

Mann, J., and Assoc. (2012). "Oil absorbent pads, rolls, socks, floor sweep, spill kits," http://www.uzrags.com/absorbents.shtml, retrieved 2013.

Mann, J., and Marrinan, H. J. (1958). "Polarized infrared spectra of cellulose-1," *J. Polymer Sci.* 27(115), 595-596.

Masoodi, R., and Pillai, K. M. (2010). "Darcy's law-based model for wicking in paper-like swelling porous media" *AIChE J.* 56(9), 2257-2267.

Masoodi, R., Pillai, K. M., and Varanasi, P. P. (2010). "Effect of externally applied liquid pressure on wicking in paper wipes," *J. Engineered Fibers Fabrics* 5(3), 49-66.

Masoodi, R., Tan, H., and Pillai, K. M. (2011). "Darcy's law-based numerical simulation for modeling 3D liquid absorption into porous wicks," *AIChE J.* 57(5), 1132-1143.

Mathavan, G. N. and Viraraghavan, T. (1992). "Coalescence/filtration of an oil-in-water emulsion in a peat bed," *Water Res.* 26, 91-98.

Matsumoto, Y., Kawakatsu, T., Nakajima, M., and Kikuchi, Y. (1999). "Visualization of filtration phenomena of a suspended solution including O/W emulsion or solid particle and membrane separation properties of the solution," *Water Res.* 33, 929-936.

Maurin, E., Clement, A., Gerardin, P., and Loubinoux, B. (1999). "A feasibility study on the use of chemically modified sawdusts bearing fatty alkyl chains for removal of oleic acid and olive-oil from water," *Holz Roh Werkstoff* 57(4), 265-266.

McCarthy, W. R., and Stratton, R. A. (1987). "Effects of drying on ASA esterification and sizing," *Tappi J.* 70(12), 117-121.

McHale, G. (2007). "Cassie and Wenzel: Were they really so wrong?" *Langmuir* 23, 8200-8205.

Meyer, E. E., Rosenberg, K. J., and Israelachvili, J. (2006). "Recent progress in understanding hydrophobic interactions," *Proc. Nat. Acad. Sci. USA* 103(43), 15739-15746.

Michel, J., Adams, E. E., Addassi, Y., Copeland, T., Greeley, M., James, B., McGee, B., Mitchelmore, C., Onishi, Y., Payne, J., Salt, D., and Wreen, B. (committee) (2005). *Oil Spill Dispersants. Efficacy and Effects*, Natural Research Council of the National Academies, The National Academies Press, Washington, DC.

Milne, A. J. B., and Amirfazli, A. (2012). "The Cassie equation: How it is meant to be used," *Adv. Colloid Interface Sci.* 170(1-2), 48-55.

Miyata, N. (1999). "Oil sorbency of sorbents prepared from Kenaf (*Hibiscus cannabinus* L.) plants," *Sen-I Gakkaishi* 55(12), 576-583.

Moellmann, J., and Grimme, S. (2010). "Importance of London dispersion effects for the packing of molecular crystals: A case study for intramolecular stacking in a bis-thiophene derivative," *Phys. Chem. Chem. Phys.* 12(30), 8500-8504.

Mohan, S. R. V., Devi, M. P., Reddy, M., Chandrasekhar, K., Juwarkar, A., and Sarma, P. N. (2011). "Bioremediation of petroleum sludge under anaerobic microenvironment: Influence of biostimulation and bioaugmentation," *Environ. Eng. Manag. J.* 10(11), 1609-1616.

Moura, F. C. C., and Lago, R. M. (2011). "Catalytic growth of carbon nanotubes and nanofibers on vermiculite to produce floatable hydrophobic "nanosponges" for oil spill remediation," *Applied Catalysis B: Environmental* 90, 436-440.

NAS (2003). *Oil in the Sea III: Inputs, Fates and Effects*, National Academy of Sciences, National Academy Press, Washington, DC.

Natarajan, A., Xie, J., Wang, S., Liu, Q., Masliyah, J., Zeng, Y., and Xu, Z. (2011). "Understanding molecular interactions of asphaltenes in organic solvents using a surface force apparatus," *J. Phys. Chem. C* 115, 16043-16051.

National Commission (2011). "The story of the Louisiana berms project," National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling,Washington, DC.

Nduka, J. K., Ezenweke, L. O., and Ezenwa, E. T. (2008). "Comparison of the mopping ability of chemically modified and unmodified biological wastes on crude oil and its lower fractions," *Bioresour. Technol.* 99(16), 7902-7905.

Nenkova, S. (2007). "Study of the sorption properties of lignin-derivatized fibrous composites for the remediation of oil polluted receiving waters," *BioResources* 2(3), 408-418.

Neumann, A. W., and Good, R. J. (1972). "Thermodynamics of contact angles. 1. Heterogeneous solid surfaces," *J. Colloid Interface Sci.* 38, 341-358.

NOAA (2010a). "NOAA's oil spill response. Using boom in response to oil spills," U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, Silver Spring, MD, NOAA fact sheet.

NOAA (2010b). "NOAA's oil spill response. Shoreline cleanup and assessment technique," U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, Silver Spring, MD, NOAA fact sheet.

NRC (2002). *Spills of Emulsified Fuels. Risks and Response*, National Research Council of the National Academies, The National Academies Press, Washington DC.

NRC (2005). *Oil Spill Dispersants*, National Research Council of the National Academies, The National Academies Press, Washington DC.

O'Fagain, C. (2003). "Enzyme stabilization – Recent experimental progress," *Enz. Microb. Technol.* 33(2-3), 137-149.

Oh, Y. S., Maeng, J., and Kim, S. J. (2000). "Use of microorganism-immobilized polyurethane foams to absorb and degrade oil on water surface," *Appl. Microbiol. Biotechnol.* 54(3), 418-423.

Oliver, J. F., Hug, C., and Mason, S. G. (1977). "Apparent contact angle of liquids on finely-grooved solid surfaces – SEM study," *J. Adhesion* 8(3), 223-234.

Orupold, K., Habicht, J., and Tenno, T. (2008). "Leaching behaviour of oil shale semicoke: Compliance with the waste acceptance criteria for landfills," *Oil Shale* 25(2), 267-275.

Ott, R. (2005). *Sound Truth and Corporate Myth$. The Legacy of the Exxon Valdez Oil Spill*, Dragonfly Sisters Press, Cordova, Alaska.

Pasichnyk, I., Everaers, R., and Maggs, A. C. (2008). "Simulating Van der Waals interactions in water/hydrocarbon-based complex fluids," *J. Phys. Chem. B* 112(6), 1761-1764.

Pasila, A. (2004). "A biological oil absorption filter," *Mar. Pollut. Bull.* 49, 1006-1012.

Pate, J. (1992). "Cotton: A renewable resource for oil spill cleanups," *Nonwovens Industry* 6, 32-35.

Payne, K. C., Jackson, C. D., Aizpurua, C. E., Rojas, O. J., and Hubbe, M. A. (2012). "Oil spills abatement: Factors affection oil uptake by cellulosic fibers," *Environ. Sci. Technol.* 46, 7725-7730.

Penela-Arenaz, M., Bellas, J., and Vazquez, E. (2009). "Effects of the Prestige oil spill on the biota of NW Spain: 5 years of learning," *Adv. Marine Biol.* 56, 365-396.

Perkovic, M., and Sitkov, A. (2008). "Oil spill modeling and combat," In: Soares, C. G., and Kolev, P. N. (eds.), *Maritime Industry, Ocean Engineering and Coastal Resources*, Vols. 1 and 2, Book Series: *Proceedings and Monographs in Engineering Water and Earth Sciences*, 1161-1169.

Perwuelz, A., De Olivera, T. N., and Caze, C. (1999). "Study of wetting at the silicone oil/water/fibre interface," *Colloids Surf. A – Physicochem. Eng. Aspects* 147(3), 317-329.

Phifer, D. W., and Costello, C. A. (1992). "Characterization of polypropylene and polyester meltblown materials used for food oil absorption," *J. Food Sci.* 57(1), 213-216.

Piao, C., Winandy, J. E., and Shupe, T. F. (2010). "From hydrophilicity to hydrophobicity: A critical review: Part I. Wettability and surface behavior," *Wood Fiber Sci.* 42(4), 490-510.

Pokhrel, D., and Viraraghavan, T. (2004). "Treatment of pulp and paper mill wastewater – A review," *Sci. Total Environ.* 333, 37-58.

Prince, R. C., Varadaraj, R., Fiocco, R. J., and Lessard, R. R. (1999). "Bioremediation as an oil spill response tool," *Environ. Technol.* 20(8), 891-896.

Pushkarev, V. V., Yuzhannov, A. G., and Men, S. K. (1980). *Treatment of Oil-Containing Wastewater*, Allterton Press, New York.

Radetic, M., Jocic, D., Jovancic, P, Petrovic, Z., and Thomas, H. (2003). "Recycled wool-based nonwoven material as an oil sorbent," *Environ. Sci. Technol.* 37(5), 1008-1012.

Raible, R. L. (1990). "Oil spill cleanup compositions," *US Pat.* 4,925,343.

Rajakovic, V., Aleksic, G., Radetic, M., and Rajakovic, L. (2007). "Efficiency of oil removal from real wastewater with different sorbent materials," *J. Hazard. Mater.* 143, 494-499.

Rajaković-Ognjanović, V., Aleksić, G., and Rajaković, L. (2008). "Governing factors for motor oil removal from water with different sorption materials," *J. Hazard. Mater.* 154, 558-563.

Rao, A. V., Hegde, H. D., and Hirashima, H. (2007). "Adsorption and desorption of organic liquids in elastic superhydrophobic silica aerogels," *J. Colloid Interface Sci.* 305, 124-132.

Rastegar, S. O., Mousavi, S. M., Shojaosadati, S. A., and Sheibani, S. (2011). "Optimization of petroleum refinery effluent treatment in a UASB reactor using response surface methodology," *J. Hazard. Mater.* 197, 26-32.

Rattanawong, O., Kaewsichan, L., Grisdanurak, N., and Yuasa, A. (2007). "Sorption of oil emulsified in water on oil palm fibers," *Korean J. Chem. Eng.* 24(1), 67-71, DOI: 10.1007/s11814-007-5011-6.

Rengasamy, R. S., Dipayan, D., and Karan, P. C. (2011). "Study of oil sorption behavior of filled and structured fiber assemblies made from polypropylene, kapok and milkweed fibers," *Journal of Hazardous Materials* 186(1), 526-532.

Rethmeier, J., and Jonas, A. (2003). "Lignite based oil binder mats: A new absorbent strategy and technology," *Spill Sci. Technol. Bull.* 8(5-6), 565-567.

Reynold, J. G., Coronado, P. R., and Hrubesh, L. W. (2001). "Hydrophobic aerogels for oil-spill clean up – Synthesis and characterization," *J. Non-Crystalline Solids* 292, 127-137.

Ribeiro, T. M. H., and Rubio, J. (1999). "Emulsified oil biosorption onto non-living biomass of *Salvinia* sp.," In: REWAS'99 Global Symposium on Recycling, Waste Treatment and Clean Technology," Gaballah, I., Hager, J., and Solozabal, R., Vols. I-III, pp. 2249-2257.

Ribeiro, T. H., Rubio, J., and Smith, R. W. (2003). "A dried hydrophobic aquaphyte as an oil filter for oil/water emulsions," *Spill Sci. Technol. Bull.* 8(5-6), 483-489.

Ribeiro, T. M. H., Smith, R. W. and Rubio, J. (2000). "Sorption of oils by nonliving biomass of a *Salvinia* sp.," *Enviorn. Sci. Technol.* 34(24), 5201-5205.

Roberts, J. K., and Orr, W. J. C. (1938). "Induced dipoles and the heat of adsorption of argon on ionic crystals," *Trans Faraday Soc.* 34, 1346-1349.

Rodriguez-Valverde, M. A., Ruiz-Cabello, F. J. M., and Cabrerizo-Vilchez, M. A. (2008). "Wetting on axially-patterned heterogeneous surfaces," *Advan. Colloid Interface Sci.* 138(2), 84-100.

Rojo, F. (2009). "Degradation of alkanes by bacteria," *Environ. Microbiol.* 11(10), 2477-2490.

Roman, M. (2009). "Model cellulosic surfaces: History and recent advances," *Model Cellulosic Surfaces*, ACS Symposium Ser., Vol. 1019, 3-53.

Rosales, P. I., Suidan, M. T., and Venosa, A. D. (2010). "A laboratory screening study on the use of solidifiers as a response tool to remove crude oil slicks on seawater," *Chemosphere* 80(4), 389-395.

Rosenholm, J. B. (2010). "Critical comparison of molecular mixing and interaction models for liquids, solutions and mixtures," *Advan. Colloid Interface Sci*. 156(1-2), 14-34.

Saez-Navarrete, C., Gelmi, C. A., Reyes-Bozo, L., and Godoy-Faundez, A. (2008). "An exploratory study of peat and sawdust as enhancers in the (bio)degradation of n-dodecane," *Biodegrad.* 19(4),: 527-534, DOI: 10.1007/s10532-007-9158-y.

Said, A. E. A. A., Ludwick, A. G., and Aglan, H. A. (2009). "Usefulness of raw bagasse for oil absorption: A comparison of raw and acylated bagasse and their components," *Bioresour. Technol.* 100(7), 2219-2222.

Saito, M., Ishi, N., Ogura, S., Maemura, S., and Suzuki, H. (2003). "Development and water tank tests of sugi bark sorbent (SBS)," *Spill Sci. Technol. Bull.* 8(5-6), 475-482.

Saiton, M., Umehara, K., Nobuya, M., Nakamura, F., Kato, J., and Endoh, H. (1996). "Process for preparing oil sorbent and device for continuously preparing the same," *US Pat.* 5,585,319.

Samokhvalov, A. (2011). "Heterogeneous photocatalytic reactions of sulfur aromatic compounds," *Chemphyschem* 12(16), 2870-2885.

Sathasivam, K., and Haris, M. R. H. M. (2010). "Adsorption kinetics and capacity of fatty acid-modified banana trunk fibers for oil in water," *Water Air Soil Pollution* 213(1-4), 413-423.

Sayed, S. A., and Zayed, A. M. (2006). "Investigation of the effectiveness of some adsorbent materials in oil spill clean-ups," *Desalination* 194(1-3), 90-100.

Schatzberg, P. (1971). *Investigations of Sorbents for Removing Oil Spills from Water,* US Coast Guard Report No. 724110.1/2/1, US Coast Guard Headquarters, Washington, DC.

Scherr, K. E., Lundaa, T., Klose, V., Bochmann, G., and Loibner, A. P. (2012). "Changes in bacterial communities from anaerobic digesters during petroleum hydrocarbon degradation," *J. Biotechnol.* 157(4), 564-572.

Scott, W. S. (1979). "Use of oil sorbent materials for small herbicide spills," *Bull Environ. Contam. Toxicol.* 23, 123-128.

Seveno, D., Blake, T. D., Goossens, S., and De Coninck, J. (2011). "Predicting the wetting dynamics of a two-liquid system," *Langmuir* 27(24), 14958-14967.

Sharma, K. R. (2011). "On centrifugal high volume separation of oil and water," 11AIChE - 2011 AIChE Annual Meeting, Conference Proceedings, 1 pp.

Silva, S. L., Silva, A. M. S., Ribeiro, J. C., Martins, F. G., Da Silva, F. A., and Silva, C. M. (2011). "Chromatographic and spectroscopic analysis of heavy crude oil mixtures with emphasis in nuclear magnetic resonance spectroscopy: A review," *Anal. Chim. Acta* 707(1), 18-37.

Silva-Tilak, V. (2002). "Method of oil cleanup using coconut coir pitch," *US Pat.* 6,391,120.

Simanzhenkov, V., and Idem, R. (2003). *Crude Oil Chemistry,* Marcel Dekker, New York, 409 pp.

Spill-kit (2012). "EnviroMet: Absorbents," http://spill-kit.com/, Retrieved 2013.

Sreekala, M. S., Goda, K., and Devi, P. V. (2008). "Sorption characteristics of water, oil and diesel in cellulose nanofiber reinforced corn starch resin/ramie fabric composites," *Composite Interfac.* 15(2-3), 281-299.

Srinivasan, A., and Viraraghavan, T. (2008). "Removal of oil by walnut shell media," *Bioresour. Technol.* 99, 8217-8220.

Srinivasan, A., and Viraraghavan, T. (2010). "Oil removal from water using biomaterials," *Bioresour. Technol.* 101(17), 6594-6600.

Stanssens, D., Van den Abbeele, H., Vonck, L., Schoukens, G., Deconinck, M., and Samyn, P. (2011). "Creating water-repellent and super-hydrophobic cellulose substrates by deposition of organic nanoparticles," *Mater. Lett.* 65(12), 1781-1784.

Stone, J. E., and Scallan, A. M. (1966). "Influence of drying on the pore structures of the cell wall," in *Consolidation of the Paper Web,* Trans. Symp. Cambridge, Sept. 1965, F. Bolam (ed.), Tech. Sec. British Paper and Board Makers' Assoc. Inc, London, Vol. 1, 145-174.

Sun, D., Jong, S. C., Duan, X. D., and Zhou, D. (1999). "Demulsification of water-in-oil emulsion by wetting coalescence materials in stirred- and packed-column," *Colloids Surf. A: Physicochem. Eng. Aspects* 150, 69-75.

Sun, D. Z., Duan, X. D., Li, W. X., and Zhou, D. (1998). "Demulsification of water-in-oil emulsion by using porous glass membrane," *J. Membrane Sci.* 146(1), 65-72.

Sun, X.-F., Sun, R., and Sun, J.-X. (2002). "Acetylation of rice straw with or without catalysts and its characterization as a natural sorbent in oil spill cleanup," *J. Agricultural Food Chem.* 50(22), 6428-6433.

Sun, X.-F., Sun, R. C., and Sun, J. X. (2003). "A convenient acetylation of sugarcane bagasse using NBS as a catalyst for the preparation of oil sorption-active materials," *J. Mater. Sci.* 38(19), 3915-3923.

Suni, S., Kosunen, A. L., Hautala, M., Pasila, A., and Romantschuk, M. (2004). "Use of a by-product of peat excavation, cotton grass fibre, as an sorbent for oil spills," *Mar. Pollut. Bull.* 49, 916-921.

Suni, S., Kosunen, A. L., and Romantschuk, M. (2006). "Microbially treated peat-cellulose fabric as a biodegradable oil-collection cloth," *J. Environ. Sci. Health. Part A – Toxic/Hazard. Subst. Environ. Eng.* 41(6), 999-1007.

Suni, S., Koskinen, K., Kauppi, S., Hannula, E., Ryynänen, T., Aalto, A., Jäänheimo, J., Ikävolko, J., and Romatschuk, M. (2007). "Removal by sorption and *in situ* biodegradation of oil spills limits damage to marine biota: A laboratory simulation," *Ambio* 36(2), 173-179.

Supplylinedirect (2012). "Universal sorbent boom," http://www.supplylinedirect.com/item/spillresponse/absorbents/universal/universalsorbentboom/

Svitova, T., Theodoly, O., Christiano, S., Hill, R. M., and Radke, C. J. (2002). "Wetting behavior of silicone oils on solid substrates immersed in aqueous electrolyte solutions," *Langmuir* 18(18), 6821-6829.

Swanson, J. W., and Cordingly, S. (1959). "Surface chemical studies of pitch. II. The mechanism of the loss of absorbency and development of self-sizing in papers made from wood pulps," *TAPPI* 42(10), 812-819.

Tao, M., Niu, J. T., and Jin, B. D. (2011). "New oil-absorbent fiber absorb the oil of water," *Adv. Civil Eng.* Pts. 1-6(255-260), 2860-2866.

Tavisto, M., Kuisma, R., Pasila, A., and Hautala, M. (2003). "Wetting and wicking of fibre plant straw fractions," *Indust. Crops Prod.* 18(1), 25-35.

Teas, C., Kalligeros, S., Zanikos, F., Stournas, S., Lois, E., and Anastopoulos, G. (2001). "Investigation of the effectiveness of absorbent materials in oil spills clean up," *Desalination* 140(3), 259-264.

Tirmizi, N. P., Raghuraman, B., and Wiencek, J. (1996). "Demulsification of water/oil/solid emulsions by hollow-fiber membranes," *AICHE J.* 42(5), 1263-1276.

Tookey, K., and Abbot, J. (1991). "Clean-up of soft sediments, phase 2 trials at Steart Flats. WSL report CR 3643. National Environmental Technology Center, AEA Technology, Culham, Abingdon, UK.

Tze, W. T., and Gardner, D. J. (2001). "Swelling of recycled wood pulp fibers: Effect on hydroxyl availability and surface chemistry," *Wood Fiber Sci.* 33(3), 364-376.

van Beilen, J. B., and Funhoff, E. G. (2007). "Alkane hydroxylases involved in microbial alkane degradation," *Appl. Microbiol. Biotech.* 74(1), 13-21.

Vanem, E., Endresen, O., and Skjong, R. (2008). "Cost-effectiveness criteria for marine oil spill preventive measures," *Reliability Eng. Sys. Safety* 93(9), 1354-1368.

Varadaraj, R., Bock, J., and Robbins, M. L. (1995b). "Bioremediation of hydrocarbon contaminated soil," *US Pat.* 5,436,160.

Varadaraj, R., and Brons, C. (1998). "Bioremediation method of hydrocarbon contaminated soils, water, and/or sludge using urea-surfactant clathrates," *US Pat.* 5,811,290.

Varadaraj, R., and Brons, C. (2007a). "Molecular origins of heavy oil interfacial activity. Part 1: Fundamental interfacial properties of asphaltenes derived from heavy crude oils and their correlation to chemical composition," *Energy Fuels* 21(1), 195-198.

Varadaraj, R., and Brons, C. (2007b). "Molecular origins of heavy crude oil interfacial activity. Part 2: Fundamental interfacial properties of model naphthenic acids and naphthenic acids separated from heavy crude oils," *Energy Fuels* 21(1), 199-204.

Varadaraj, R., and Brons, C. (2007c). “Molecular origins of crude oil interfacial activity. Part 3: Characterization of the complex fluid rag layer formed at crude oil-water interfaces,” *Energy Fuels* 21(3), 1617-1621.

Varadaraj, R., and Brons, C. (2012d). “Molecular origins of crude oil interfacial activity. Part 4: Oil-water interface elasticity and crude oil asphaltene films,” *Energy Fuels* 26(12), 7164-7169.

Varadaraj, R., Robbins, M. L., Bock, J., Pace, S., and MacDonald, D. (1995a). “Dispersion and biodegradation of oil spills on water,” In: Proceedings of the 1995 International Oil Spill Conference, Long Beach, California, American Petroleum Institute, Washington, D.C., pp. 101-106.

Varadaraj, R., and Savage, D. W. (1998). “Phytoadditives for enhanced soil bioremediation,” *US Pat.* 5,716,839.

Varghese, K., and Cleveland, T. G. (2008). “Kenaf as a deep-bed filter medium to remove oil from oil-in-water emulsions,” *Separation Sci. Technol.* 33(14), 2197-2220.

Visser, J. (1972). “On Hamaker constants: A comparison between Hamaker constants and Lifshitz-van der Waals constants,” *Advan. Colloid Interface Sci.* 3, 331-363.

Vogler, E. A. (1998). “Structure and reactivity of water at biomaterial surfaces,” *Advan. Colloid Interface Sci.* 74, 69-117.

Walters, M. L. (2002). “Aromatic interactions in model systems,” *Current Opin. Chem. Biol.* 6(1), 736-741.

Wang, J., Lu, Q., Harbottle, D., Sjöblom, J., Xu, Z., and Zeng, H. (2012). “Molecular interactions of a polyaromatic surfactant C5Pe in aqueous solutions studied by a surface forces apparatus,” *J. Phys. Chem. B* 116, 11187-11196.

Wang, S. H., Li, M., and Lu, Q. H. (2010). “Filter paper with selective absorption and separation of liquids that differ in surface tension,” *ACS Applied Materials & Interfaces* 2(3), 677-683.

Wardlaw, G. D., Arey, J. S., Reddy, C. M., Nelson, R. K., Ventura, G. T., and Valentine, D. L. (2008). “Disentangling oil weathering at a marine seep using GCxGC: Broad metabolic specificity accompanies subsurface petroleum biodegradation,” *Environ. Sci. Technol.* 42(19), 7166-7173.

Washburn, W. (1921). “The dynamics of capillary flow,” *Phys. Rev.* 17, 273-283.

Wasser, R. B. (1987). “The reactivity of alkenyl succinic anhydride: Its pertinence with respect to alkaline sizing,” *J. Pulp Paper Sci.* 13(1), J29-J32.

Wei, Q. F., Mather, R. R., Fotheringham, A. R., and Yang, R. D. (2003). “Evaluation of nonwoven polypropylene oil sorbents in marine oil-spill recovery,” *Marine Pollution Bulletin* 46, 780-783.

Wennerstrom, H. (2003). “The van der Waals interaction between colloidal particles and its molecular interpretation,” *Colloids Surg. A – Physicochem. Eng. Aspects* 228, 189-195.

Wenzel, R. N. (1936). “Resistance of solid surfaces to wetting by water,” *Ind. Eng. Chem.* 28, 988-994.

Witka-Jezewska, E., Hupka, J., and Pieniazek, P. (2003). “Investigation of oleophilic nature of straw sorbent conditioned in water,” *Spill Sci. Technol. B* 8(5-6), 561-564.

Wolcott, M. P., and Shutler, E. L. (2003). “Temperature and moisture influence on compression-recovery behavior of wood,” *Wood Fiber Sci.* 35(4), 540-551.

Xia, Y. Q., and Boufadel, M. C. (2010). “Lessons from the Exxon Valdez oil spill disaster in

Alaska," *Disaster Adv.* 3(4), 270-273.

Yakimov, M. M. Golyshin, P. N., Lang, S., Moore, E. R., Abraham, W. R., Lundsorf, H., and Timmis, K. N. (1998). "*Alcanivorax borkumensis* gen. nov., sp. nov., a new hydrocarbon-degrading and surfactant producing marine bacterium," *Int. J. Syst. Bacteriol.* 48, 339-348.

Yamamoto, H. (1998). "Manufacturing of oil sorbent from heat treated wood fiber and developing new products," *Cellulose Commun.* 5, 148-151.

Yamane, C., Aoyagi, T., Ago, M., Sato, K., Okajima, K., and Takahashi, T. (2006). "Two different surface properties of regenerated cellulose due to structural anisotropy," *Polymer J.* 38(8), 819-826.

Yang, Y., Zhang, X., and Wang, Z. (2002). "Oilfield produced water treatment with surface-modified fiber ball media filtration," *Water Sci. Technol.* 46(11-12), 165-170.

Yeboah, N. N. N., and Burns, S. E. (2011). "Geological disposal of energy-related waste," *KSCE J. Civil Eng.* 15(4), 697-705.

Young, T. (1805). "An essay on the cohesion of fluids," *Phil. Trans. Royal Soc. London* 95,

Zahid, M. A., Halligan, J. E., and Johnson, R. F. (1972). "Oil slick removal using matrices of polypropylene filaments," *Indust. Eng. Chem. Process Des. Dev.* 11(4), 550-558.

Zaidi, A., Simms, K., and Kok, S. (1992). "The use of micro/ultrafiltration for the removal of oil and suspended solids from oilfield brines," *Water Sci. Tech.* 25(10), 163-176.

Zaritsky, A., Wang, P., and Vischer, N. O. E. (2011). "Instructive simulation of the bacterial cell division cycle," *Microbiol.-SGM* 157, 1876-1885.

Zeinalipour-Yazdi, C. D., and Pullman, D. P. (2006). "Correlation of polarizabilities with Van Der Waals interactions in pi-systems," *J. Phys. Chem. B* 1100(47), 24260-24265.

Zhu, Q., Pan, Q. M., and Liu, F. T. (2011a). "Facile removal and collection of oils from water surfaces through superhydrophobic and superoleophilic sponges," *J. Phys. Chem. C* 115(35), 17464-17470.

Zhu, R. Z., Cui, S. W., and Wang, X. S. (2010). "Theoretical foundation of Zisman's empirical equation for wetting of liquids on solid surfaces," *Eur. J. Phys.* 31(2), 251-256.

Zhu, Z., Li, J., Xie, S., and Yuan, G. (2011b). "Research and application on resource utilization technology of oily waste drilling fluid," *Petrol. Sci. Technol.* 29(14), 1470-1481.

Zisman, W. A. (1972). "Surface energetics of wetting, spreading, and adhesion," *J. Paint Technol.* 44(564), 41-57.

Zou, C. S., Luo, G. S., Sun, Y., and Dai, Y. Y. (2003). "Mechanism of coalescence demulsification with microfiltration membrane," *Chinese J. Chem. Eng.* 11(3), 344-347.

Zouboulis, A. I., and Avranas, A. (2000). "Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation," *Colloids Surf. A: Physicochem. Eng. Aspects* 172, 153-161.

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APPENDIX

Table A. Tabulation of Research Publications for Removal of Oils from Water by Use of Raw or Modified Lignocellulosic Materials (See notes below table for key to abbreviations)

Emulsion?	Oil type	Sorbent class	Sorbent type	Dry? Wet?	Modification	Bulk density (g/cm3)	Assembly	Sorption Capacity (g/g)	Regenerated?	Loss on reuse	Key Findings	Author (year)
Not	Diesel	Bio	Kapok fib.	D	-	0.02-0.08	L	37 11	Y	22	Packing density important	Abdullah *et al.* 2010
Not	Used diesel	Bio	Kapok fib.	D	-	0.02-0.08	L	50 12	Y	22	Packing density important	Abdullah *et al.* 2010
Not	Motor oil	Bio	Kapok fib.	D	-	0.02-0.08	L	47 12	Y	22	Packing density important	Abdullah *et al.* 2010
O/W	Palm oil	Bio	Chitosan powder	W	Deace-tylated	-	L	2-3	-	-	Sorption isotherms; second-order rate	Ahmad *et al.* 2005a
Not	Crude	Syn	Recycled tire rubber	W	-	-	L	3-5	-	-	Fresh & marine water, helped fish survival	Aisien *et al.* 2006
Not	Heavy crude	Bio	Sisal	L	-	-	L	3-7	-	-	Fine ground fraction had higher capacity	Annunciado *et al.* 2005
Not	Heavy crude	Bio	Leaves residues	L	-	-	L	1-3	-	-		Annunciado *et al.* 2005
Not	Heavy crude	Bio	Sawdust	L	-	-	L	4-7	-	-		Annunciado *et al.* 2005
Not	Heavy crude	Bio	Coir fiber	L	-	-	L	2-6	-	-		Annunciado *et al.* 2005

Emulsion?	**Oil type**	**Sorbent class**	**Sorbent type**	**Dry? Wet?**	**Modification**	**Bulk density** (g/cm3)	**Assembly**	**Sorption Capacity (g/g)**	**Regenerated?**	**Loss on reuse**	**Key Findings**	**Author (year)**
Not	Heavy crude	Bio	Sponge gourd	L	-	-	L	2-5	-	-		Annunciado *et al.* 2005
Not	Heavy crude	Bio	*Ceiba speciosa*	L	-	-	L	80-90	-	-	Silk floss tree of South America	Annunciado *et al.* 2005
Not	Light Heavy Gasoil Light Heavy Gasoil	Bio	Bagasse Rice hull	L	-	-	L	3-6 5-6 4-5 4 5 4	-	-	Sorbent materials were placed in a net bag.	Bayat *et al.* 2005
O/W	Cutting oil	Bio	Sawdust	W	-	0.78	PB	-	-	-	Filtration conditions optimized.	Cambiella *et al.* 2010
O/W	Various	Bio	Solid white pine wood	W	-	-	-	0.1-0.6	-	-	Water, limonene, various micro-emulsions	Carillo *et al.* 2012
Not	Hexa-decane	Bio	Nanocell. aerogel	W	Silan-ated	0.004-0.014	L	45	Y	-	Freeze-dried material sorbed oil and shed water.	Cervin *et al.* 2012
Not	LC	Bio	Cotton	L	-	-	NW	31	Y	25	Waxy surface	Choi 1996
Not	LC	Bio	Cotton	L	bleach	-	NW	7	Y	30	-	Choi 1996
Not	LC	Bio	Wool	L	-	-	NW	30	Y	-		Choi 1996
Not	LC	Bio	Kapok	L	-	-	NW	37	Y	-		Choi 1996
Not	LC	Bio	Milkweed	L	-	-	NW	40	Y	-		Choi 1996
Not	LC	Bio	Kenaf	L	-	-	NW	7	Y	-		Choi 1996
Not	LC	Syn	PP	L	-	-	NW	13	Y	5		Choi 1996
Not	LC	Bio	Milkweed	M	-	-	L	30-34	-	-	Water soaking decreased sorption morately.	Choi & Cloud 1992

Emulsion?	Oil type	Sorbent class	Sorbent type	Dry? Wet?	Modification	Bulk density (g/cm3)	Assembly	Sorption Capacity (g/g)	Regenerated?	Loss on reuse	Key Findings	Author (year)
Not	LC	Bio	Cotton	M	-	-	L	32-35	-	-		Choi & Cloud 1992
Not	LC	Syn	Poly-propylene	M	-	-	L	8-10	-	-		Choi & Cloud 1992
Not	LC	Mix	Milkweed & polypropyl.	M	-	-	L	25-27	-	-		Choi & Cloud 1992
	LC				-		NP	-	-	-		Choi *et al.* 1993
Not	Male-thion	Bio	Cotton	M	-	-	NW	35	Y	85	Gray, unmod. cotton	Choi *et al.* 1994
Not	Male-thion	Bio	Cotton	M	bleach	-	NW	3-7	-	-		Choi *et al.* 1994
Not	Male-thion	Syn	PP	M	-	-	-	24	Y	0	Sorption actually increased with reuse	Choi *et al.* 1994
Not	Oil	Syn	PDMS sponge	D	-	0.18-0.75	Sp	4-10	Y	-	Simple squeezing	Choi *et al.* 2011
	1-MCP		Plant tissue		-	-	-	-	-	-	Drying decreased sorption	Choi & Huber 2009
O/W	Olive mill	Bio	Pine sawdust	W	-	-	-	-	-	-	Did not attempt to quantify sorbed amount.	Chouchene *et al.* 2010
O/W	Olive mill	Bio	Pine sawdust	W	Ground Sieved	-	-	-	-	-	Did not attempt to quantify sorbed amount.	Chouchene *et al.* 2012
Not	Motor oil	Bio	Peat	D	Dried	-	L	13-16	-	-	Drainage time effects; wicking between particles	Cojocaru *et al.* 2011
Not	Diesel	Bio	Peat	D	Dried	-	L	9-12	-	-		Cojocaru *et al.* 2011
Not	Light fuel oil	Bio	Peat	D	Dried	-	L	12-14	-	-		Cojocaru *et al.* 2011

Emulsion?	**Oil type**	**Sorbent class**	**Sorbent type**	**Dry? Wet?**	**Modification**	**Bulk density** (g/cm3)	**Assembly**	**Sorption Capacity (g/g)**	**Regenerated?**	**Loss on reuse**	**Key Findings**	**Author (year)**
Not	3 oils	Bio	Peat	L	Dried	-	L	Var.	-	-	Result not calculated based on g/g; models only	Cojocaru *et al.* 2011
Not	Veget oil	Bio	Cotton	L	Bleached	-	P	20	Y	40	Squeezing, sorbent cake prepared by squeezing	Deschamps *et al.* 2003a
Not	Veget oil	Bio	Cotton	L	-	-	P	30	-	-		Deschamps *et al.* 2003a
Not	Mineral oil	Bio	Cotton	L	-	-	P	30	-	-		Deschamps *et al.* 2003a
Not	Fuel oil	Bio	Cotton	L	-	-	P	30	-	-		Deschamps *et al.* 2003a
Not	Crude oil	Bio	Cotton	L	-	-	P	30	-	-		Deschamps *et al.* 2003a
O/W	Veget oil	Bio	Cotton	W	Acyla-tion	-	L	19	-	-	Octanoic acid esterification; packed bed column	Deschamps *et al.* 2003b
Not	CCl_4	Syn	Cyclodextrin	D	-	-	L	11-79	Ex	5	Cross-linking decreased capacity greatly	Ding *et al.* 2011
Not	$CHCl_3$	Syn	Cyclodextrin	D	-	-	L	14-73	Ex	5	Cross-linking decreased capacity greatly	Ding *et al.* 2011
Not	Xylene	Syn	Cyclodextrin	D	-	-	L	17-44	Ex	5	Cross-linking decreased capacity greatly	Ding *et al.* 2011
Not	Toluene	Syn	Cyclodextrin	D	-	-	L	19-46	Ex	5	Cross-linking decreased capacity greatly	Ding *et al.* 2011
O/W	Oil		Tree bark	W	Metal ions	-	L	0.2-2	-	-	Deisel, hydraulic, heavy alcohol, oilic acid	Haussard *et al.* 2003

Emulsion?	Oil type	Sorbent class	Sorbent type	Dry? Wet?	Modification	Bulk density (g/cm3)	Assembly	Sorption Capacity (g/g)	Regenerated?	Loss on reuse	Key Findings	Author (year)
Not	Xylene	Syn	Cyclodextrin copol. beads	D	-	-	L	75	-	-		He *et al.* 2012
Not	CCl_4	Syn	Cyclodextrin copol.beads	D	-	-	L	102	-	-		He *et al.* 2012
Not	Oil	Bio	Kapok	M	Dried	-	L	40	-	-		Hori *et al.* 2000
Not	Diesel oil	Bio	Kapok	M	-	-	PB	-	-	-	Showed strong ability to clean up water.	Huang & Lim 2006
Not	Hydraulic	Bio	Kapok	M	-	-	PB	-	-	-		Huang & Lim 2006
Not	Crude oil	Bio	Barley straw	M	Dried	-	L	9-12	Y	70	Simple squeezing	Husseien *et al.* 2009b
Not	Crude oil, etc	Bio	Carbonized pith bagass	L	-	-	L	14-20	Y	50	Seven-day aged oil layers	Husseien *et al.* 2009c
Not	Heavy oil		Carbonized fir wood	D	-	0.005-0.10	L	5-80	Y	20	Packing density critical; suction to de-oil	Inagaki *et al.* 2002a
Not			Carbonized fir wood		-	-	Y	20	-	-		Inagaki *et al.* 2002b
O/W	Olive oil	Bio	Sawdust	W	Sieved	-	L	-	-	-	Oil mill wastewater; focus on air emissions	Jeguirim *et al.* 2012
Not	Crude oil		Cotton	W	-	-	L	40	Y	30	Waxy surface, small denier; squeezing	Johnson *et al.* 1973
Not	Motor oil	Bio	Kapok fiber	M	Dried	-	L	0.8	-	-	Time effects.	Khan *et al.* 2004
Not	Motor oil	Bio	Cattail fiber	M	Dried	-	L	1.1	-	-		Khan *et al.* 2004

Emulsion?	**Oil type**	**Sorbent class**	**Sorbent type**	**Dry? Wet?**	**Modification**	**Bulk density** (g/cm3)	**Assembly**	**Sorption Capacity (g/g)**	**Regenerated?**	**Loss on reuse**	**Key Findings**	**Author (year)**
Not	Motor oil	Bio	*Salvinia* sp.	M	Dried	-	L	0.9	-	-		Khan *et al.* 2004
Not	Motor oil	Syn	Polyester fiber	M	Dried	-	L	1.0	-	-		Khan *et al.* 2004
Not	Motor oil	Bio	Wood chips	M	Dried	-	L	0.3	-	-		Khan *et al.* 2004
Not	Motor oil	Bio	Rice husk	M	Dried	-	L	0.3	-	-		Khan *et al.* 2004
Not	Motor oil	Bio	Coconut husk	M	Dried	-	L	0.06	-	-		Khan *et al.* 2004
Not	Motor oil	Bio	Bagasse	M	Dried	-	L	0.02	-	-		Khan *et al.* 2004
Not		bio	Milkweed floss		-	-	-	18-24	-	-		Knudsen 1990
Not	Paraffin oil	Bio	Nanocellul. aerogels	L	-	-	Sp	30	-	-	Floats, resists water	Korhonen *et al.* 2011
Not	HC	Bio	Carbonized rice husk	D	-	-	L	6	-	-	Less than 1.5 g water/g	Kumagai *et al.* 2007
Not	Diesel	bio	Cotton		None	-	-	31	-	-	Lumens intact	Lee *et al.* 2007
Not	Diesel	Bio	Cotton		Ground	-	-	1	-	-	Broken open	Lee *et al.* 2007
Not	Diesel	Bio	Cotton		Extrac	-	-	28	-	-	Hydrophilic	Lee *et al.* 2007
Not	Miner-al oils	Bio	Paper sludge	L	Heat, h-phob	-	L	2-7	-	-	Floats on water, aborbs oil	Likon *et al.* 2011
Not	Diesel	Bio	Kapok	D	-	0.02-0.09	L	36	Y	30	Packing density critical	Lim & Huang 2007a
Not	Hydr-aulic	Bio	Kapok	D	-	0.02-0.09	L	43	-	-		Lim & Huang 2007a

Emulsion?	**Oil type**	**Sorbent class**	**Sorbent type**	**Dry? Wet?**	**Modification**	**Bulk density** (g/cm3)	**Assembly**	**Sorption Capacity (g/g)**	**Regenerated?**	**Loss on reuse**	**Key Findings**	**Author (year)**
Not	HD40	Bio	Kapok	D	-	0.02-0.09	L	45	-	-		Lim & Huang 2007a
Not	Motor oil	Syn	PP	D	Fiber	-	P	48	Y	30	Composite of PP & rubber also worked well	Lin *et al.* 2010
Not	Motor oil	Syn	Tire rubber	D	Powder	-	P	3	Y	0		Lin *et al.* 2010
Not		Bio	Bagasse w fatty acids		Ester	-			-	-		Ludwick *et al.* 2003
O/W	Oleic acid	Bio	Sawdust	W	-	-	L	27	-	-		Maurin *et al.* 1999
O/W	Olive oil	Bio	Sawdust	W	-	-	L	32	-	-		Maurin *et al.* 1999
O/W	Oleic acid	Bio	Sawdust w fatty azides	W	Ester	-	L	40-47	-	-		Maurin *et al.* 1999
O/W	Olive oil	Bio	Sawdust w fatty azides	W	Ester	-	L	40-46	-	-		Maurin *et al.* 1999
Not		Bio	Kenaf bast fibers		Heated or not	-	-	12-33	-	-		Miyata 1999
Not		Bio	Kenaf core fibers		Heated or not	-	-	8-30	-	-		Miyata 1999
Not		Bio	Wood		-	-	-	20	-	-		Miyata 1999
Not	Crude oil	Bio	Lignin/wood composites	D	-	-	P	2-5	-	-	Time effect on amount drained off	Nenkova 2007
Not	Light crude	Syn	PU foam	L	Micro-organ.	-	-	7-9	-	-	Oil-degrading ability helped by immobilization.	Oh *et al.* 2000
Not	No. 2 fuel oil	Bio	Grasses, hemp	D	Ground	0.08-0.21		2-4	-	-	Sorbed just 1-3 g water/g; Drain time effects	Pasila 2004

Emulsion?	Oil type	Sorbent class	Sorbent type	Dry? Wet?	Modification	Bulk density (g/cm3)	Assembly	Sorption Capacity (g/g)	Regenerated?	Loss on reuse	Key Findings	Author (year)
Not	Lubricat oil	Bio	Grasses, hemp	D	Ground	0.08-0.21		2-4	-	-	Sorbed just 1-3 g water/g; Drain time effects	Pasila 2004
Not	Crude oil	Bio	Bleached SW kraft	D	-	-	L	6	-	-	Dry hydrobilic fibers sorb dry oil effectively.	Payne *et al.* 2012
Not	Crude oil	Bio	Bleached SW kraft	D	ASA	-	L	5-6	-	-	Aklylation slightly hurt sorption of oil on dry fibers.	Payne *et al.* 2012
Not	Crude oil	Bio	Bleached SW kraft	D	Lignin	-	L	7	-	-	Lignin deposition promoted oil sorption by dry fibers.	Payne *et al.* 2012
Not	Crude oil	Bio	Bleached HW kraft	D	-	-	L	5-6	-	-	Hardwood fibers were a bit less effective than SW.	Payne *et al.* 2012
Not	Crude oil	Bio	CTMP	D	-	-	L	5-6	-	-	Mechanical fibers were quite effective, both dry & wet.	Payne *et al.* 2012
Not	Crude oil	Bio	Bleached SW kraft	W	-	-	L	1.7	-	-	Wet hydrobilic fibers don't sorn oil effectively.	Payne *et al.* 2012
Not	Crude oil	Bio	Bleached SW kraft	W	ASA	-	L	2-6	-	-	Alkylation definitely helped oil sorption onto wet fibers.	Payne *et al.* 2012
Not	Crude oil	Bio	Bleached SW kraft	W	Lignin	-	L	1-6	-	-	Lignin deposition helped oil sorption onto wet fibers.	Payne *et al.* 2012
Not	Crude oil	Bio	Bleached HW kraft	W	-	-	L	1-5	-	-	-	Payne *et al.* 2012
Not	Crude oil	Bio	CTMP	W	-	-	L	4-5	-	-	Mechanical fibers were quite effective, both dry & wet.	Payne *et al.* 2012
Not	Food oils	Syn	PP meltblown	D	-	-	Y	0.33	-	-	Whicking mechanism	Phifer & Costello 1992
Not	Food oils	Syn	Polyester	D	-	-	Y	0.25	-	-		Phifer & Costello 1992
Not	Food oils	Bio	Paper towels	D	-	-	Y	0.24	-	-		Phifer & Costello 1992

Emulsion?	Oil type	Sorbent class	Sorbent type	Dry? Wet?	Modification	Bulk density (g/cm3)	Assembly	Sorption Capacity (g/g)	Regenerated?	Loss on reuse	Key Findings	Author (year)
Not	SN 150	Bio	Wool non-woven	M	Needle-punch	-	NW	14-15	Y	30		Radetic *et al.* 2003
Not	Diesel	Bio	Wool non-woven	M	Needle-punch	-	NW	12-13	-	-		Radetic *et al.* 2003
Not	Crude	Bio	Wool non-woven	M	Needle-punch	-	NW	11-12	-	-		Radetic *et al.* 2003
O/W	Motor oil	Bio	Wool	M	Carded	-	L, NW	5-6	-	-		Rajakovic *et al.* 2007
Not	Motor oil		Natural wool	M	Carded	-	NW	33	-	-		Rajakovic-O. *et al.* 2008
Not	Motor oil		Recycled wool	M	Carded	-	NW	18	-	-		Rajakovic-O. *et al.* 2008
O/W	Palm oil	Bio	Palm empty fruit bunch	W	-	-	L	0	-	-	Langmuir fits.	Rattanawong *et al.* 2007
O/W	Palm oil	Bio	Palm empty fruit bunch	W	Silanes	-	L	0.8	-	-	Langmuir fits.	Rattanawong *et al.* 2007
Not	High-dens.	Syn	PP	D	Blends	0.01-0.09	PB	10-85	-	-	Packing dens. critical, mixing w/ water hurt sorption ~10%	Rengasamy *et al.* 2011
Not	High-dens.	Bio	Kapok	D	-	0.01-0.09	PB	7-62	-	-		Rengasamy *et al.* 2011
Not	High-dens.	Bio	Milkweed	D	-	0.01-0.09	PB	5-44	-	-		Rengasamy *et al.* 2011
Not	Diesel	Syn	PP	D	Blends	0.01-0.09	PB	9-45	-	-		Rengasamy *et al.* 2011
Not	Diesel	Bio	Kapok	D	-	0.01-0.09	PB	6-53	-	-		Rengasamy *et al.* 2011
Not	Diesel	Bio	Milkweed	D	-	0.01-0.09	PB	5-37	-	-		Rengasamy *et al.* 2011

Emulsion?	Oil type	Sorbent class	Sorbent type	Dry? Wet?	Modification	Bulk density (g/cm3)	Assembly	Sorption Capacity (g/g)	Regenerated?	Loss on reuse	Key Findings	Author (year)
Not	Crude oils. 2	Syn	Silica aerogel	M	Fluorinated	-	L	237	-	-	Did not pick up any water	Reynold *et al.* 2001
Not	Crude oil	Bio	Aquatic plant *Salvinia*		Dried, ground	-	L	5-12	-	-		Ribeiro *et al.* 2000
Not	Crude oil	Bio	Peat		Dried, ground	-	L	3	-	-		Ribeiro *et al.* 2000
Not	Mineral oil	Bio	Aquatic plant *Salvinia*		Dried, ground	-	L	4-9	-	-		Ribeiro *et al.* 2000
Not	Mineral oil	Bio	Peat		Dried, ground	-	L	3	-	-		Ribeiro *et al.* 2000
O/W	Heavy crude	Bio	Aquatic plant *Salvinia*	W	Dried	-	L	7	-	-		Ribeiro *et al.* 2003
O/W	Mineral	Bio	Aquatic plant *Salvinia*	W	Dried	-	L	8-12	-	-		Ribeiro *et al.* 2003
O/W	Heavy crude	Bio	Peat	W	Dried	-	L	3	-	-		Ribeiro *et al.* 2003
O/W	Mineral	Bio	Peat	W	Dried	-	-	3	-	-		Ribeiro *et al.* 2003
Not	Oil	Bio	Bagasse	D	-	-	L	6	-	-		Said *et al.* 2009
Not	Oil	Bio	Bagasse grafted ester	D	Fatty acid	-	L	4	-	-		Said *et al.* 2009
Not	Bunkr A	Bio	Sugi bark	D	-	-	L	13	-	-	Commercialized	Saito *et al.* 2003

Emulsion?	**Oil type**	**Sorbent class**	**Sorbent type**	**Dry? Wet?**	**Modification**	**Bulk density** (g/cm3)	**Assembly**	**Sorption Capacity (g/g)**	**Regenerated?**	**Loss on reuse**	**Key Findings**	**Author (year)**
-	Motor oils		Banana fiber		Oleic acid +	-	-		-	-		Sathasivam & Haris 2010
Not	Oil		Sludge		Heat,	-	-	0.4-1.3	-	-		Sayed & Zayed 2006
Not			Garlic, onion peels		-	-	-	0.4-0.5	-	-		Sayed & Zayed 2006
Not	BC	Min	Class avg.	W	-	-	L	9	-	-		Schatzberg 1971
Not	BC	Bio	Class avg.	W	-	-	L	11	-	-		Schatzberg 1971
Not	BC	Syn	Class avg.	W	-	-	L	62	-	-		Schatzberg 1971
Not	BC	Syn	Class avg.	W	-	-	F	28	-	-		Schatzberg 1971
Not	BC	Misc	Class avg.	W	-	-	L	12	-	-		Schatzberg 1971
Not	HC	Min	Class avg.	W	-	-	L	8	-	-		Schatzberg 1971
Not	HC	Bio	Class avg.	W	-	-	L	9	-	-		Schatzberg 1971
Not	HC	Syn	Class avg.	W	-	-	L	56	-	-		Schatzberg 1971
Not	HC	Syn	Class avg.	W	-	-	F	25	Y	0		Schatzberg 1971
Not	HC	Misc	Class avg.	W	-	-	L	10	-	-		Schatzberg 1971
Not	LC	Min	Class avg.	W	-	-	L	3	-	-		Schatzberg 1971
Not	LC	Bio	Class avg.	W	-	-	L	6	-	-		Schatzberg 1971
Not	LC	Syn	Class avg.	W	-	-	L	52	-	-		Schatzberg 1971
Not	LC	Syn	Class avg.	W	-	-	F	17	-	-		Schatzberg 1971
Not	LC	Misc	Class avg.	W	-	-	L	6	-	-		Schatzberg 1971
Not	#2	Min	Class avg.	W	-	-	L	3	-	-		Schatzberg 1971
Not	#2	Bio	Class avg.	W	-	-	L	5	-	-		Schatzberg 1971
Not	#2	Syn	Class avg.	W	-	-	L	47	-	-		Schatzberg 1971
Not	#2	Syn	Class avg.	W	-	-	F	14	Y	0		Schatzberg 1971
Not	#2	Misc	Class avg.	W	-	-	L	4	-	-		Schatzberg 1971
Not	Avg	Min	Class avg.	W	-	-	L	6	-	-		Schatzberg 1971

Emulsion?	Oil type	Sorbent class	Sorbent type	Dry? Wet?	Modification	Bulk density (g/cm3)	Assembly	Sorption Capacity (g/g)	Regenerated?	Loss on reuse	Key Findings	Author (year)
Not	Avg	Bio	Class avg.	W	-	-	L	8	-	-		Schatzberg 1971
Not	Avg	Syn	Class avg.	W	-	-	L	54	-	-		Schatzberg 1971
Not	Avg	Syn	Class avg.	W	-	-	F	21	-	-		Schatzberg 1971
Not	Avg	Misc	Class avg.	W	-	-	L	8	-	-		Schatzberg 1971
Not	245-T, 24D	-	3M sheets	L	-	-	P	-	-	-	Critical to minimize time between spill and sorption.	Scott 1979
Not	Mineral oil	Bio	Walnut shells	B	-	-	L	0.6	Y	-	Squeezing	Srinivasan & V. 2008
Not	Veg. oil	Bio	Walnut shells	B	-	-	L	0.6	Y	-		Srinivasan & V. 2008
Not	Cutting oil	Bio	Walnut shells	B	-	-	L	0.7	Y	-		Srinivasan & V. 2008
O/W	Mineral oil	Bio	Fungal biomass	M	-	-	L	0.08	-	-		Srinivasan & V. 2010
O/W	Veg. oil	Bio	Fungal biomass	M	-	-	L	0.09	-	-		Srinivasan & V. 2010
O/W	Cutt-ing oil	Bio	Fungal biomass	M	-	-	L	0.08	-	-		Srinivasan & V. 2010
Not	Machine oil	Bio	Straw ester	M	Acetyl-ated	-	L	17-24	Y	-	Squeezing	Sun *et al.* 2002
Not	Machine oil	Bio	Sugar cane bagasse	M	Acetyl-ated	-	L	11-19	Y	-	Squeezing	Sun *et al.* 2003
Not	Gaso-line	Bio	Cotton grass fiber	D	-	0.01-0.04	P	13-19	-	-	Cotton grass sheds water better than most biosorbants	Suni *et al.* 2004
Not	Diesel	Bio	Cotton grass fiber	D	-	0.01-0.04	P	9-20	-	-		Suni *et al.* 2004
Not	Synth oil	Bio	Cotton grass fiber	D	-	0.01-0.04	P	11-22	-	-		Suni *et al.* 2004

Emulsion?	Oil type	Sorbent class	Sorbent type	Dry? Wet?	Modification	Bulk density (g/cm3)	Assembly	Sorption Capacity (g/g)	Regenerated?	Loss on reuse	Key Findings	Author (year)
Not	Mineral oil	Bio	Cotton grass fiber	D	-	0.01-0.04	P	14-20	-	-		Suni *et al.* 2004
Not	Motor oil	Bio	Whatman paper fiber	D	-	-	Cl	1	N	-	Whatman paper fiber only	Suni *et al.* 2006
Not	Motor oil	Bio	Peat/cellulose fabric	D	Microb culture	-	Cl	3-4	N	-	Microbially treated; 4-10% peat & Whatman paper	Suni *et al.* 2006
Not	Diesel	Bio	Cotton grass	L	-	-	L	12-23	-	-	Mussels protected even when sorbent left in water	Suni *et al.* 2007
Not	Diesel	Syn	PP	L	-	-	L	5-7	-	-		Suni *et al.* 2007
Not	Crude oil	Syn	PP nonwovens	L	-	-	NW	5-9	-	-	North Sea oil; time affect amount drained	Wei *et al.* 2003
Not	Crude oil	Syn	Tire rubber	D	As is	-	L	10	-	-		Wu & Zhou 2009
Not	Crude oil	Syn	Tire rubber	D	DVB	-	L	25	-	-	Derivatization effective	Wu & Zhou 2009
Not	Crude oil	Syn	PP filaments	L	-	-	P	4-6	-	-	Wave action, spacing between strands	Zahid *et al.* 1972
Not	Lubri-cating	Syn	Superhydro phobic	L	PU do-decan	-	Sp	19	Y	60	Squeezing	Zhu *et al*. 2011
Not	Oct-ane	Syn	Superhydro phobic	L	PU do-decan	-	Sp	13	Y	10	Squeezing	Zhu *et al*. 2011
Not	Dec-ane	Syn	Superhydro phobic	L	PU do-decan	-	Sp	13	Y	20	Squeezing	Zhu *et al*. 2011
Not	Dode-cane	Syn	Superhydro phobic	L	PU do-decan	-	Sp	14	Y	35	Squeezing	Zhu *et al*. 2011

Notes for Table A

Emulsion?

Not	Not emulsified
OW	Oil-in-water emulsion
WO	Water-in-oil emulsion

Oil type

BC	Bunker C low-grade fuel oil
C	Crude oil, unspecified
HC	Heavy crude (*e.g.* from Venezuela)
LC	Light crude (*e.g.* south Louisiana)
MO	Mineral oil

Sorbent Classes

AC	Activated carbon
Ag	Agricultural residue
Bio	Cellulosic biomass
Min	Mineral
Misc	Miscellaneous
Rub	Rubber, as from recycled tires
Syn	Synthetic fibers, *e.g.* polypropylene

Dry? Wet?

B	Sorbent tested BOTH with dry oil & layer of oil floating on water, with similar results
D	DRY sorbent added to DRY oil
H	Heated (above 50 ^{o}C) to dry
L	Sorbent added to LAYER of oil floating on water
M	Oil was being MIXED in water with agitation
W	Sorbent soaked in WATER before oil sorption

Bulk Density

Units	g/cm^3

Assembly

PB	Packed bed
F	Foam
L	Loose fibers
NP	Needlepunched
P	Pad, unspecified
Sp	Sponge

Regenerated

Ex	Extracted
Y	Yes (generally by squeezing)

Loss on Reuse

Percentage decline relative to first use, after several cycles