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

Martin A. Hubbe, Orlando J. Rojas, Merv Fingas, and Bhupender S. Gupta

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

Contact information: a: Department of Forest Biomaterials, North Carolina State University, Campus Box 8005, Raleigh, NC 27695-8005; b: Aalto Univ., Dept. Forest Products Technology, FI-02015 Espoo, Finland; c: Spill Science, 1717 Rutherford Point, Edmonton, AB, T6W 1J6; d: Department of Textile Engineering, Chemistry, and Science, North Carolina State University, Campus Box 8301; Raleigh, NC 27695; * Corresponding author: hubbe@ncsu.edu

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

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.

Current 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

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

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

<table>
<thead>
<tr>
<th>Skimmer Type</th>
<th>Recovery Rate (m³/h) *</th>
<th>Percent Oil**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light Crude</td>
<td>Heavy Crude</td>
</tr>
<tr>
<td>Oleophilic Skimmers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>disc</td>
<td>0.2 to 2</td>
<td>0.2 to 10</td>
</tr>
<tr>
<td>brush drum</td>
<td>0.5 to 20</td>
<td>0.5 to 2</td>
</tr>
<tr>
<td>brush belt</td>
<td>15 to 30</td>
<td>1 to 10</td>
</tr>
<tr>
<td>drum</td>
<td>0.5 to 30</td>
<td></td>
</tr>
<tr>
<td>belt</td>
<td>1 to 20</td>
<td>3 to 20</td>
</tr>
<tr>
<td>rope mop</td>
<td>2 to 20</td>
<td>2 to 10</td>
</tr>
<tr>
<td>Weir Skimmers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>small weir</td>
<td>0.5 to 5</td>
<td>2 to 20</td>
</tr>
<tr>
<td>large weir</td>
<td>30 to 100</td>
<td>5 to 10</td>
</tr>
<tr>
<td>Elevating Skimmers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>paddle conveyer</td>
<td>1 to 10</td>
<td>1 to 20</td>
</tr>
<tr>
<td>Submersion Skimmers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>large</td>
<td>1 to 80</td>
<td>1 to 20</td>
</tr>
<tr>
<td>Suction Skimmers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>small</td>
<td>0.3 to 2</td>
<td></td>
</tr>
<tr>
<td>large trawl unit</td>
<td>2 to 40</td>
<td></td>
</tr>
<tr>
<td>large vacuum unit</td>
<td>3 to 20</td>
<td>3 to 10</td>
</tr>
</tbody>
</table>

* 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.

Treatying 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. Simanzhkenkov and Idem (2003) estimated that 1 kg of light oil will typically spread to cover up to 12,000 m² 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**

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

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)**

<table>
<thead>
<tr>
<th>Sorbent Type</th>
<th>All Data Combined</th>
<th>Kapok, Milkweed, &amp; Cotton</th>
<th>Hydrophobized Biomass</th>
<th>Other Biomass</th>
<th>Synthetic Fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>10</td>
<td>30</td>
<td>12</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>Mean</td>
<td>17</td>
<td>28</td>
<td>18</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>Minimum</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>Maximum</td>
<td>102</td>
<td>62</td>
<td>47</td>
<td>90</td>
<td>102</td>
</tr>
<tr>
<td>Count</td>
<td>340</td>
<td>47</td>
<td>24</td>
<td>150</td>
<td>70</td>
</tr>
</tbody>
</table>

* 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 $\gamma_c$ 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 $\gamma_c$ and sorption characteristics (Piao et al. 2010). In particular, lower values of $\gamma_c$ 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 $\gamma_c$ 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 $\gamma_c$, 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 (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 °C, then with further treatment at 500 °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 physicochemical 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)](image-url)

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. 2011).
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**

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Light Crude</th>
<th>Heavy Crude</th>
<th>Heavy Fuel</th>
<th>Olive Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>mPa.s at 15 °C</td>
<td>5 to 50</td>
<td>50 to 50,000</td>
<td>50,000</td>
<td>50 to 200</td>
</tr>
<tr>
<td>Density</td>
<td>g/mL at 15 °C</td>
<td>0.78 to 0.88</td>
<td>0.88 to 1.00</td>
<td>0.96 to 1.04</td>
<td>0.91 to 0.916</td>
</tr>
<tr>
<td>Flash Point</td>
<td>°C</td>
<td>-30 to 30</td>
<td>-30 to 60</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>Ppm</td>
<td>10 to 50</td>
<td>5 to 30</td>
<td>1 to 5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Pour Point</td>
<td>°C</td>
<td>-40 to 30</td>
<td>-40 to 30</td>
<td>5 to 20</td>
<td>-10 to 0</td>
</tr>
<tr>
<td>Interfacial Tension</td>
<td>mN/m at 15 °C</td>
<td>10 to 30</td>
<td>15 to 30</td>
<td>25 to 35</td>
<td>30 to 35</td>
</tr>
</tbody>
</table>
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 °C, with an additional gradual increase as the temperature was raised further to 50 °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)
- $\pi-\pi$ 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 (Simanzenkov 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 cellullosic 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 \( \pi-\pi \) 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.

\( \pi \) 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 \( \pi \) electrons, giving rise to an attraction (Mahadevi and Sastry 2012; Lu et al. 2013). Frontera et al. (2011) have reviewed the subject of \( \pi \) 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 \( \pi \) interactions with charged groups is typically less important than hydrogen bonding (see later). The contribution of \( \pi \) 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 \( \pi-\pi \) 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 \(-\text{OH}\) 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.

\[ F_{\text{net}} = F_{\text{electrostatic}} + F_{\text{hydrogen bonding}} + F_{\text{van der Waals}} \]  

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>
<thead>
<tr>
<th>Concept</th>
<th>Selected References</th>
</tr>
</thead>
<tbody>
<tr>
<td>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, <em>e.g.</em> adsorbed on a surface.</td>
<td>Adamson &amp; Gast 1997</td>
</tr>
<tr>
<td>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).</td>
<td>Adamson &amp; Gast 1997; Roman 2009</td>
</tr>
<tr>
<td>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.</td>
<td>Johnson and Dettre 1969; Roman 2009</td>
</tr>
<tr>
<td>The presence of small pores in a cellulosic substrate can be expected to result in relatively large hysteresis effects (see previous item).</td>
<td>Cassie &amp; Baxter 1944; Denesuk <em>et al.</em> 1994</td>
</tr>
<tr>
<td>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.</td>
<td>Payne <em>et al.</em> 2012</td>
</tr>
<tr>
<td>The presence of water on a cellulosic surface does not necessarily impede spreading of oil on that surface.</td>
<td>Payne <em>et al.</em> 2012</td>
</tr>
</tbody>
</table>

**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),

\[ \gamma_{SA} = \gamma_{SO} + \gamma_{OA} \cos \theta \]  

Hubbe *et al.* (2013). “Cellulosic oil-spill sorbents,” *BioResources* 8(2), Pg #s to be added 24
where $\gamma_{SA}$ is the interfacial tension between the solid and air, $\gamma_{SO}$ is the interfacial tension between the solid and oil, $\gamma_{OA}$ is the interfacial tension between the oil and the air, and $\theta$ 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 $\theta$ is less than 90°, the fluid will spread, and the surface will be considered “wettable.” By contrast, when $\theta$ 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)](image-url)

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 $\theta$ (Adamson and Gast 1997). Strategies to achieve this condition can be predicted by rearranging Eq. 2 as follows (Hubbe et al. 2012b):

$$\cos \theta = \frac{\gamma_{SA} - \gamma_{SO}}{\gamma_{OA}}$$ (3)

$$\theta = \arccos \left\{ \frac{\gamma_{SA} - \gamma_{SO}}{\gamma_{OA}} \right\}$$ (4)

In addition to the surface energy terms already defined above, researchers have found it useful to use the critical surface tension $\gamma_c$ 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 $\gamma_c$ is determined for the desired solid with a set of homologous fluids that have different surface tensions, $\gamma_L$. 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 $\gamma_c$ for the solid. The concept of critical surface tension implies that a fluid of the series with a surface tension less than $\gamma_c$, 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.

![Diagram of Young's equation](image)

**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.*, 

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

\[ \theta = \arccos \left\{ \frac{\gamma_{SW} - \gamma_{SO}}{\gamma_{OW}} \right\} \]  
(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 \(\gamma_{SW}\) term because the partially hydrogen bondable cellulotic phase is facing water. Meanwhile, the value of the \(\gamma_{OW}\) term typically would be somewhat lower than that of \(\gamma_{OA}\) due to significant London dispersion interactions expected between the oil and aqueous phases (and almost no such interaction with air). Regarding the \(\gamma_{SO}\) 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:

\[
\begin{align*}
    r \gamma_{SA} & = r \gamma_{SO} + \gamma_{OA} \cos \theta, \quad \text{or} \\
    \gamma_{SA} & = \gamma_{SO} + (\gamma_{OA} \cos \theta) / r
\end{align*}
\]

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.

Advancing & Receding Angles on a Rough Surface

![Advancing & Receding Angles on a Rough Surface](image)

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

Hubbe et al. (2013). “Cellulosic oil-spill sorbents,” BioResources 8(2), Pg #s to be added
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,

\[ \cos \theta_{a,p} = f_1 \cos \theta - f_2 \]  

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.

\[ \cos \theta_1 = f_1 \cos \theta - f_2 \]

\[ f_2 < 1 ; \ f_1 + f_2 \geq 1 \]

\[ \cos \theta_2 = f_1 \cos \theta + f_2 \]

**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 $\gamma_{OA}$, 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](image)

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 $\eta$. 

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l = \frac{\eta t}{\gamma_{OA}}$</td>
<td>Linear relationship under ideal conditions</td>
</tr>
</tbody>
</table>

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Hubbe et al. (2013). “Cellulosic oil-spill sorbents,” *BioResources* 8(2), Pg #s to be added 29
\[ \frac{dl}{dt} = \gamma_{OA} R \cos \theta / (4 \eta l) \]  
\[ l = [\gamma_{OA} R t \cos \theta / (2 \eta)]^{0.5} \]  

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):

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

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), \( \gamma \) is the fluid surface tension (dynes/cm), \( \theta \) is the contact angle (radians), \( \eta \) is the fluid viscosity (dynes.sec/cm\(^2\)), \( \rho \) 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 (\( \gamma_{WA} \)) and oil-air (\( \gamma_{OA} \)) 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):

\[ R = \left[ \frac{d}{2 \pi B_0} \left\{ \frac{T A}{W} - \frac{1}{\rho} \right\} \right]^{1/2} \]  

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 \( (9 \times 10^5) \). 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, $\gamma_{OA}$, can be interesting for a number of reasons. First, the only practical way to change the value of $\gamma_{OA}$ 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 $\gamma_{OA}$, 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 $\theta$ 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 $\eta_O$ and $\eta_W$ 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.

\[
\frac{dl}{dt} = \frac{\gamma_{OA} R \cos \theta}{(4 \eta_O l_O + 4 \eta_W l_W)}
\]  

(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 \( \gamma_{SW} \) 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; Koltuneiwiwiz 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. (Kotuneiwiwiz 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. Simanekov 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.

Inoculation

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 m² 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


Hubbe et al. (2013). “Cellulosic oil-spill sorbents,” BioResources 8(2), Pg #s to be added.


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


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

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)

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

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

Hubbe et al. (2013). “Biosorption of oil; Appendix, Table A,” *BioResources* 8(2), ####-####.
<table>
<thead>
<tr>
<th>Emulsion?</th>
<th>Oil type</th>
<th>Sorbent class</th>
<th>Sorbent type</th>
<th>Dry? Wet?</th>
<th>Modification</th>
<th>Bulk density (g/cm³)</th>
<th>Assembly</th>
<th>Sorption Capacity (g/g)</th>
<th>Regenerated?</th>
<th>Loss on reuse</th>
<th>Key Findings</th>
<th>Author (year)</th>
</tr>
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<tbody>
<tr>
<td>Not</td>
<td>LC</td>
<td>Bio</td>
<td>Cotton</td>
<td>M</td>
<td>-</td>
<td>L</td>
<td>32-35</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Choi &amp; Cloud 1992</td>
</tr>
<tr>
<td>Not</td>
<td>LC</td>
<td>Syn</td>
<td>Polypropylene</td>
<td>M</td>
<td>-</td>
<td>L</td>
<td>8-10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Choi &amp; Cloud 1992</td>
</tr>
<tr>
<td>LC</td>
<td>-</td>
<td>NP</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Choi et al. 1993</td>
</tr>
<tr>
<td>Not</td>
<td>Malethion</td>
<td>Bio</td>
<td>Cotton</td>
<td>M</td>
<td>-</td>
<td>NW</td>
<td>35</td>
<td>Y</td>
<td>85</td>
<td>Gray, unmod. cotton</td>
<td></td>
<td>Choi et al. 1994</td>
</tr>
<tr>
<td>Not</td>
<td>Malethion</td>
<td>Bio</td>
<td>Cotton</td>
<td>M</td>
<td>bleach</td>
<td>NW</td>
<td>3-7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Choi et al. 1994</td>
</tr>
<tr>
<td>Not</td>
<td>Malethion</td>
<td>Syn</td>
<td>PP</td>
<td>M</td>
<td>-</td>
<td>-</td>
<td>24</td>
<td>Y</td>
<td>0</td>
<td>Sorption actually increased with reuse</td>
<td>Choi et al. 1994</td>
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</tr>
<tr>
<td>Not</td>
<td>Oil</td>
<td>Syn</td>
<td>PDMS sponge</td>
<td>D</td>
<td>-</td>
<td>Sp</td>
<td>4-10</td>
<td>Y</td>
<td>-</td>
<td>Simple squeezing</td>
<td>Choi et al. 2011</td>
<td></td>
</tr>
<tr>
<td>1-MCP</td>
<td>Plant tissue</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Drying decreased sorption</td>
<td>Choi &amp; Huber 2009</td>
<td></td>
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<tr>
<td>O/W</td>
<td>Olive mill</td>
<td>Bio</td>
<td>Pine sawdust</td>
<td>W</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Did not attempt to quantify sorbed amount.</td>
<td>Chouchene et al. 2010</td>
<td></td>
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<td>Bio</td>
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<td>Ground Sieved</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Did not attempt to quantify sorbed amount.</td>
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<tr>
<td>Not</td>
<td>Motor oil</td>
<td>Bio</td>
<td>Peat</td>
<td>D</td>
<td>Dried</td>
<td>L</td>
<td>13-16</td>
<td>-</td>
<td>-</td>
<td>Drainage time effects; wicking between particles</td>
<td>Cojocaru et al. 2011</td>
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<tr>
<td>Not</td>
<td>Diesel</td>
<td>Bio</td>
<td>Peat</td>
<td>D</td>
<td>Dried</td>
<td>L</td>
<td>9-12</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Cojocaru et al. 2011</td>
<td></td>
</tr>
<tr>
<td>Not</td>
<td>Light fuel oil</td>
<td>Bio</td>
<td>Peat</td>
<td>D</td>
<td>Dried</td>
<td>L</td>
<td>12-14</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Cojocaru et al. 2011</td>
<td></td>
</tr>
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</table>

Hubbe et al. (2013). “Biosorption of oil; Appendix, Table A,” *BioResources* 8(2), ####-####.
<table>
<thead>
<tr>
<th>Emulsion?</th>
<th>Oil type</th>
<th>Sorbent class</th>
<th>Sorbent type</th>
<th>Dry? Wet?</th>
<th>Modification</th>
<th>Bulk density (g/cm³)</th>
<th>Assembly</th>
<th>Sorption Capacity (g/g)</th>
<th>Regenerated?</th>
<th>Loss on reuse</th>
<th>Key Findings</th>
<th>Author (year)</th>
</tr>
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<tr>
<td>Not</td>
<td>3 oils</td>
<td>Bio</td>
<td>Peat</td>
<td>L</td>
<td>Dried</td>
<td>-</td>
<td>L</td>
<td>Var.</td>
<td>-</td>
<td>-</td>
<td>Result not calculated based on g/g; models only</td>
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</tr>
<tr>
<td>Not</td>
<td>Veget oil</td>
<td>Bio</td>
<td>Cotton</td>
<td>L</td>
<td>Bleached</td>
<td>-</td>
<td>P</td>
<td>20</td>
<td>Y</td>
<td>40</td>
<td>Squeezing, sorbent cake prepared by squeezing</td>
<td>Deschamps et al. 2003a</td>
</tr>
<tr>
<td>Not</td>
<td>Veget oil</td>
<td>Bio</td>
<td>Cotton</td>
<td>L</td>
<td>-</td>
<td>P</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Deschamps et al. 2003a</td>
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<td>P</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
<td>P</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>Deschamps et al. 2003a</td>
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</tr>
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<td>Crude oil</td>
<td>Bio</td>
<td>Cotton</td>
<td>L</td>
<td>-</td>
<td>P</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Deschamps et al. 2003a</td>
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<td>Cotton</td>
<td>W</td>
<td>Acylation</td>
<td>-</td>
<td>L</td>
<td>19</td>
<td>-</td>
<td>-</td>
<td>Octanoic acid esterification; packed bed column</td>
<td>Deschamps et al. 2003b</td>
</tr>
<tr>
<td>Not</td>
<td>CCl₄</td>
<td>Syn</td>
<td>Cyclodextrin</td>
<td>D</td>
<td>-</td>
<td>L</td>
<td>11-79</td>
<td>Ex</td>
<td>5</td>
<td>-</td>
<td>Cross-linking decreased capacity greatly</td>
<td>Ding et al. 2011</td>
</tr>
<tr>
<td>Not</td>
<td>CHCl₃</td>
<td>Syn</td>
<td>Cyclodextrin</td>
<td>D</td>
<td>-</td>
<td>L</td>
<td>14-73</td>
<td>Ex</td>
<td>5</td>
<td>-</td>
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<td>Ding et al. 2011</td>
</tr>
<tr>
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<td>Xylene</td>
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<td>Cyclodextrin</td>
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<td>L</td>
<td>17-44</td>
<td>Ex</td>
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<td>-</td>
<td>Cross-linking decreased capacity greatly</td>
<td>Ding et al. 2011</td>
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<tr>
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<td>Toluene</td>
<td>Syn</td>
<td>Cyclodextrin</td>
<td>D</td>
<td>-</td>
<td>L</td>
<td>19-46</td>
<td>Ex</td>
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<td>-</td>
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<td>Ding et al. 2011</td>
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<td>O/W</td>
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<td>Tree bark</td>
<td>Metal ions</td>
<td>W</td>
<td>-</td>
<td>L</td>
<td>0.2-2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Diesel, hydraulic, heavy alcohol, olic acid</td>
<td>Haussard et al. 2003</td>
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Hubbe et al. (2013). “Biosorption of oil; Appendix, Table A,” BioResources 8(2), #####-#####.
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<td>Hardwood fibers were a bit less effective than SW.</td>
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<td>Mechanical fibers were quite effective, both dry &amp; wet.</td>
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Hubbe et al. (2013). “Biosorption of oil; Appendix, Table A,” *BioResources* 8(2), ####-####.
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## Table A

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<th>Sorbent type</th>
<th>Dry? Wet?</th>
<th>Modification</th>
<th>Bulk density (g/cm³)</th>
<th>Assembly</th>
<th>Sorption Capacity (g/g)</th>
<th>Regenerated?</th>
<th>Loss on reuse</th>
<th>Key Findings</th>
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**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 °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

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Hubbe *et al.* (2013). “Biosorption of oil; Appendix, Table A,” *BioResources* 8(2), ####-####.
**Bulk Density**

| Units | g/cm³ |

**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