Cotton Fiber-Based Sorbents for Treating Crude Oil Spills

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ABSTRACT: Wood and plant fibers have been studied as natural sorbent materials for treating aquatic oil spills; however, the effectiveness of these materials is limited by their tendency to absorb water as well as oil. Chemical pretreatment of cotton fibers with fatty acids was examined as a means of enhancing the performance of cotton as a sorbent for crude oil. A raw cotton fiber was chemically modified with C18 fatty acid by simple leaving group chemistry. Free surface hydroxyl groups were modified with long alkyl chains to create fibers that displayed increased water contact angles, indicative of a significant decrease in surface energy. The increased affinity for oil and corresponding repulsion of water on the individual modified fibers translated to greater sorption of oil and rejection of water by loose assemblies of fibers (i.e., balls or yarn) when compared with unmodified cotton. X-ray diffraction (XRD) pattern, Fourier transform infrared (FT-IR), 13C cross-polarization/magic angle spinning solid-state nuclear magnetic resonance (CP/MAS SSNMR), and scanning electron microscopy (SEM) showed that cotton fibers were significantly exfoliated by the intercalation of C18 fatty acids about 2.4 times in its diameter. In the presence of seawater, the highly oleophilic C18 fatty acid-modified cotton fiber showed a maximum oil sorption capacity of 35.58 g per gram of fiber, about ~49% greater than that of the corresponding raw cotton fiber.

INTRODUCTION

Oil has been a major energy source for the last several decades, but accidental spills have resulted in major environmental concerns and threats to human health.1 Active responses to oil spills in open water include the use of sorbents, dispersants, skimming, herders, booms, and in situ burning.2 Sorption and skimming can allow for the capture and recovery of the oil, thus reducing the amount of pollutants remaining in the environment.2 Sorbents with oleophilicity, hydrophobicity, and oil retention/recovery capacity could be effective for both thick slicks and thin sheens under a range of weather conditions. Organic sorbent materials have potential desirability as the oiled sorbent must ultimately be cleaned or disposed of, and organic sorbents may be allowed to degrade with residual oil back on shore.3

Many scientific efforts have demonstrated methods for enhancing the beneficial properties of natural organic sorbent materials.4,5 Natural sorbent materials such as rice hull, wood cotton, and kenaf are attractive for oil spill sorbents due to their high oil sorption capacity, biodegradability, and cost-effectiveness.6,7 In the case of raw cotton, low micronaire (air permeability of compressed fibers) cotton, which is composed of smaller diameter fibers, showed higher crude oil sorption than that of high micronaire cotton (thicker fibers) because the finer fiber provides more accessible sites for surface adsorption and inter-fiber capillary sorption.8,9–10 Synthetic polymeric sorbents such as polypropylene, polystyrene fiber, and polyurethane generally have high oil sorption capacity,11–13 but they are made from oil byproducts and expensive resources.14 Some other superhydrophobic resin materials have also been developed, but these are nonrenewable and have complicated preparation process that release hazardous byproducts.15

Many scientists have demonstrated the replacement of free surface hydroxyl groups of natural sorbents with alkyl groups to enhance their hydrophobicity and oleophilicity. Simple acetylation of free hydroxyl groups in the presence of catalysts or in the absence of catalysts is the most effective method to modify the surface, but the short acetyl groups are sometimes insufficient to render an entire surface hydrophobic,18 which is indirectly evident from the very low weight percent gain (WPG) following acetylation (<5.0 wt %).19,20 In contrast, long alkyl groups add more significantly to the surface area of the sorbent polymer and therefore have greater potential to increase hydrophobicity on the sorbent surface. Fatty acids are also promising antibacterial agents that destabilize bacterial cell membranes, causing a range of direct and indirect inhibitory effects.21,22 Therefore, fatty acid-modified cotton fiber sorbents can be stored for extended periods and may have increased stability and activity in wet and nutrient-rich conditions.

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Many efforts to modify natural sorbents using fatty acids with long alkyl chains have been conducted. However, a simple replacement reaction of hydroxyl groups with fatty acids in the presence of acid catalysts led to competitive dehydration on the cellulose surface because hydroxyl nucleophiles on the solid surface are not very effective in these conditions. Our previous work demonstrated that the attachment of a good leaving group on a cellulose surface followed by replacement with fatty acid was highly effective and led to high weight percent gain using a low-temperature reaction process.\(^{23,24}\) Sawdust modified in this manner with mixed fatty acids showed enhanced crude oil sorption capacity and very high contact angles with water.

In this study, we report a simple method to modify the surface of cotton fiber with C18 fatty acid using a 50 °C oven. Exposed hydroxyl groups on cotton fiber were modified with C18 fatty acids to produce a very hydrophobic surface. The modified cotton fibers were easily separated from the reaction mixture, which was heterogeneous, and showed about 50% enhanced crude oil sorption capacity relative to that of raw cotton fiber. Structural, chemical, thermal, and surface characterization of the modified fibers provide insight into the mechanism(s) underpinning the enhanced sorption capacity.

### RESULTS AND DISCUSSION

Untreated cotton fiber contains wax, which makes the fiber naturally hydrophobic, but the wax is coated rather than chemically bonded. Table 1 summarizes the physical properties of the raw and modified cotton fiber samples.

| Table 1. Physical Properties of the Raw and Modified Cotton Fiber Samples |
| --- |
| | raw cotton fiber | modified cotton fiber |
| cellulose content (%) | 94.22 | 43.04 |
| density (g/cm³) | 1.528 ± 0.005 | 1.066 ± 0.008 |
| WPG (%) | n/a | 132.36 |
| moisture sorption (%)\(^{a}\) | 3.92–4.22 | 0.13–0.21 |
| sizes (mm) | 12–32 | 11–28 |
| accessible OH content (mol/kg) | 16.93 | 2.81 |
| Brunauer–Emmett–Teller (BET) surface area (m²/g) | 70.72 | 50.15 |

\(^{a}\)Measured in a K₂CO₃ chamber (43.2 ± 0.4% RH) at 20 °C for 24 h.

of the raw and modified cotton fiber samples used in this study. A simple extraction method can determine wax content on the cotton fiber, and it is usually about 0.6–13 wt %.\(^{25,26}\) The raw cotton fiber we used in this study contained 5.78% of impurities including wax. The high ratio of cellulose content (96.22%) of the raw cotton fiber was chemically modified with the C18 chain (43.04% cellulose). The chemical inclusion of large amounts of C18 chains into cotton fibers led to a significant decrease in density (1.528 → 1.066 g/cm³). The accessible OH content of the cotton fiber was 16.93 mol/kg, which is 91.5% of the theoretical maximum accessible OH group content (18.5 mol/kg),\(^{22}\) and 83.4% of accessible OH groups in the cotton fiber were chemically modified with C18 chains. When the cotton fiber was modified with C18 fatty acid followed by washing with dichloromethane and drying at 60 °C overnight, the weight percent gain (WPG) was 132.36%. The hydrophobic property of the modified cotton fiber was demonstrated by a moisture sorption test in a K₂CO₃ chamber at 20 °C. The moisture sorption (3.92–4.22%) of the cotton fiber was significantly decreased to 0.13–0.21% for the modified cotton fiber.

The increase in hydrophobicity was further confirmed using water contact angle measurements. The water contact angle of the raw cotton fiber was 110.70 ± 3.77°. However, the substantial enhancement of the hydrophobic character of the surface of the modified cotton fiber was clearly observed by an increase in θ with the polar water: 138.10 ± 0.76°. The surface energy of each fiber sample was determined using the Owens/Wendt model (eq 1)\(^{27}\)

\[ \frac{1 + \cos \theta}{2} \times \sqrt{\gamma_p^l} = \sqrt{\gamma_p^s} \times \sqrt{\gamma_p^d} + \sqrt{\gamma_d^d} \]  

where \(\gamma_p^s\) and \(\gamma_p^d\) are the polar and dispersive components of surface tension of liquids, respectively. The subscripts s and l represent solid and liquid, respectively, and superscripts p and d represent polar and dispersive components of surface free energy, respectively. Surface energies and their components for each of the fibers were obtained from the slope and intercept of the fitting line using three different liquids. The surface tensions of liquids are listed in Table 2.\(^{24}\) The total surface energy of each sample is the summation of the polar \(\gamma_p^s\) and the dispersive \(\gamma_p^d\) parts according to

\[ \gamma = \gamma_p^s + \gamma_p^d \]  

Figure 1a shows the surface energies calculated from contact angles with water, ethylene glycol, and diiodomethane.\(^{27}\) There is an obvious difference in surface energy observed between the two surfaces. The surface energy of the raw cotton fiber was 37.73 mJ/m² (polar 2.90, dispersive = 34.83 mJ/m²) and that of the modified cotton fiber was 26.53 mJ/m² (polar = 3.39, dispersive = 23.14 mJ/m²). Both numbers are far below the surface tension of water (72.8 mN/m), which indicates that both surfaces are likely to repel water molecules. To compare both surfaces by wetting characteristics in detail, the wetting envelope was plotted as shown Figure 1b. Surface energy and its polar and dispersive components play important roles for fibers used as a sorbent to absorb oil from a water surface.\(^{29}\) Higher surface energy substrates are more easily wetted than lower energy substrates. At low surface energy with a dominant dispersive component, where affinities between oil molecules and the fiber surface are much higher than that between water molecules and the fiber surface, oils are easily absorbed into fibers, while water molecules are repelled outside the fiber assembly due to a high energy barrier. Therefore, wetting with water molecules is less likely using the modified cotton fiber surface than the raw cotton fiber surface. The selective sorption of oil and rejection of water allows a smaller mass of sorbent to be used to collect oil and therefore reduces the overall mass of saturated sorbent collected during the treatment of a spill. Furthermore, this
reduces the amount of water that must also be separated from the oil/water mix collected by the sorbent following the recovery of the saturated sorbent.

The X-ray diffraction (XRD) patterns of the raw and modified cotton fiber samples were measured, as shown in Figure 2a. For a typical cellulose I crystalline structure of raw cellulose fiber, the diffraction planes of 101, 101', 002, and 040 at 2θ are 15.0, 16.2, 22.3, and 35.0°, respectively. The modified cotton fiber showed significantly reduced intensity in three diffraction planes, 101, 101', and 040, and although the (002) diffraction peak was maintained, it showed a significant broadening and exfoliation after the modification with C18 fatty acid. A d-spacing (002) of the raw cotton fiber used in this study was 3.92 Å. It was significantly increased (4.39 Å) when modified with C18 fatty acid, indicating that the substitution of hydroxyl groups by C18 fatty acids breaks both inter- and intramolecular hydrogen bonds of cellulose and decreases the degree of crystallinity.30,31 The crystallinity index determined in this study was >40.0% for the raw cotton fiber and ~2.0% for the modified cotton fiber. This indicates that the crystallinity of the modified cotton fiber is significantly decreased by the intercalation of amorphous fatty acid molecules.

FT-IR spectra support the formation of chemical bonds between C18 fatty acids and hydroxyl groups on the cotton fiber. This was observed by enhancement of the carbonyl (C=O, red arrow) peak at 1740 cm⁻¹ and an increase in the intensity of the C–H band (blue arrow) at 2850–2950 cm⁻¹ arising from the aliphatic acid chain (Figure 2b). It was also observed that the single band at 2850–2950 cm⁻¹ in the raw cotton fiber was changed to double absorptive bands in the modified cotton fiber. The decrease in the intensity (from raw cotton to modified cotton) of the broadband around 3300
cm\(^{-1}\), assigned to the cellulose O–H vibration (black arrow), is additional proof of the successful esterification of cotton fibers.

Thermal properties of the raw and modified cotton fibers were determined to understand their weight loss at 150 °C, initial decomposition temperature \(T_{d,1}\) and decomposition temperature at maximum degradation rates \(T_{d,1}\) and \(T_{d,2}\) (shown in Figure 3a and Table 3). It was observed that the weight loss at the initial temperature (150 °C) significantly decreased after the surface modification. This is attributed to a lower moisture content of the modified cotton fiber due to the substitution with hydrophobic fatty acid. The modified cotton fiber started to decompose at 183 °C, which was a significantly lower temperature than that of the raw cotton fiber (273 °C). The lower thermal stability of the crystallinity is associated with the substitution of cotton hydroxyls with fatty acids. The thermogravimetry (TG) plots of both samples showed two main separate degradation steps, with maximum degradation temperatures, \(T_{d,1}\) and \(T_{d,2}\), where \(T_{d,1}\) was assigned to the cellulose fraction and \(T_{d,2}\) was attributed to the fatty acid fraction. The \(T_{d,1}\) of the modified cotton fiber (218 °C) was dramatically lowered from that of the raw cotton fiber (346 °C) due to the exfoliation of the crystalline cellulose network with C18 fatty acid.

\(^{13}\)C cross-polarization magic angle spinning nuclear magnetic resonance (\(^{13}\)C CP/MAS NMR) spectra of the raw and modified cotton fiber samples were taken to prove the chemical bonding of C18 fatty acid to the cotton fiber surface (Figure 3b).\(^{32}\) The raw cotton fiber is lignin-free so that there is only a broad cellulose network (50–150 ppm), which is not well resolved due to the composite of cellulose and hemicellulose. It contains a natural oxidized carbon resonance at 165.78 ppm. For the modified cotton fiber, there are four new resonances at 13.79, 25.02, 30.53, and 172.08 ppm, which are associated with an alkyl hydrocarbon chain (three different chemical shifts) and carbonyl carbon from the esterification reaction of C18 fatty acid, respectively. All chemical shifts of C18 fatty acid were assigned according to the literature and previous records.\(^{33,34}\) The carbonyl carbon was shifted and enhanced after the chemical reaction with C18 fatty acid.

Table 3. Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric (DTG) Data for the Raw and Modified Cotton Fiber Samples

| sample                  | weight loss at 150 °C (%) | \(T^\circ\) at 50% weight loss | \(T_{d,1}\) °C | \(T_{d,2}\) °C | \(T_{d,3}\) °C |
|-------------------------|---------------------------|----------------------------------|----------------|----------------|----------------|
| raw cotton fiber        | 4.211                      | 339                             | 273            | 346            | 431            |
| modified cotton fiber   | 0.892                      | 275                             | 183            | 218            | 518            |

Figure 4. SEM images of the (a, b) raw cotton fiber and (c, d) the modified cotton fiber.
To enable a rapid response to a spill, large quantities of sorbents need to be prepared in advance and stored for months or years at strategic locations prior to use. A potential challenge for sorbent materials that are based upon natural materials is that they may be susceptible to biodegradation or biologically mediated alteration of their properties during storage. The potential spoilage of the modified cotton fiber sample was investigated by testing in a closed water system at 18 °C. Natural fibers including cellulose are more susceptible to microorganisms such as fungi and bacteria than many synthetic fibers due to microorganisms that produce enzymes capable of converting cellulose to soluble sugar. Factors that affect biological deterioration are humidity, temperature, pH, and air circulation. In nonsterile water, a dark color change indicated that the raw cotton fiber had become heavily colonized by microorganisms in 15 days, and the cotton also started to get wet. The brown color became black and covered the entire surface in 10 months; however, the modified cotton fiber sample remained clean and dry, maintaining its hydrophobicity even after 10 months (Figure 5). While not an exhaustive analysis, this suggests that the modified cotton fiber could have advantages for storing in humid and salty conditions over raw cotton fiber samples.

Figure 5. Spoilage (microbial colonization) of the (a–c) raw and (d–f) modified cotton fibers: (a, d) 15 days, (b, e) 3 months, and (c, f) 10 months.

Figure 6. (a) Time-dependent crude oil sorption and (b) comparative reusability of the raw and modified cotton fibers (crude oil concentration = 50 mL/500 mL of seawater at 20 °C).

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Figure 6a shows the time-dependent crude oil sorption plots of both raw and modified cotton fiber samples. Raw cotton fiber, which is inherently waxy and hydrophobic, sorbed crude oil quickly and reached a plateau corresponding to its sorption capacity of about 23.89 g crude oil in 2 min. The C18 fatty acid-modified cotton fiber also reached its sorption capacity of 35.58 g crude oil in 2 min. The sorption capacity of the modified fiber was enhanced by 48.93% relative to that of the raw cotton fiber. Both raw and modified cotton fiber samples were also tested for their ability to be reused. Each sample underwent multiple cycles (sorption, washed with dichloromethane to remove crude oil, vacuum-dried), and both showed very consistent sorption capacities with 4.9−9.5% deviation (Figure 6b).

**CONCLUSIONS**

A raw cotton fiber is naturally hydrophobic, though it still absorbs water and is susceptible to microbial spoilage. To enhance its use as an oil sorbent, cotton was modified with stearic acid by a simple process and tested as a sorbent for treating crude oil spills. The C18 fatty acid-modified cotton fiber was highly hydrophobic, oleophilic, and had excellent buoyancy in seawater, and its sorption capacity was...
substantially enhanced relative to that of the raw cotton fiber. The maximum crude oil sorption capacity of the modified cotton fiber was 35.58 g/g material, which was enhanced by about ~49% greater than that of the raw cotton fiber. The quantitative and visual analysis demonstrated that the cotton fiber was exfoliated and thickened by the chemical infiltration of C18 alkyll chains of the fatty acids, and that the alkyll chains protected deformation of the cellulose network in water. The highly hydrophobic modified cotton fiber has a much lower surface free energy (23.14 mJ/m²) than that of the raw cotton fiber (34.83 mJ/m²), indicating why oil is more easily absorbed on the fiber than water. Modification of cotton was simple and inexpensive, yielding a product with high stability, rapid sorption, high crude oil capacity, low water retention, and significant reusability. Like natural cotton, the modified cotton fiber could be fabricated into a variety of forms (ropes, pillows, mats) for ease of use. These features suggest that this treatment process and the modified cotton fiber provide a very promising alternative sorbent for crude oil spill response.

**EXPERIMENTAL METHODS**

**Chemicals and Materials.** All chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. Cotton fibers were purchased from a local craft store (Richland, WA).

**Modification of Raw Cotton Fiber.** For the esterification reaction of raw cotton fiber with stearic acid (C18 fatty acid), 5.0 g of p-TsCl was dissolved in 100 mL of pyridine, then 2.0 g of raw cotton fiber mat was added to this mixture. The reaction bottle was placed inside an oven (50 °C), and 6.0 g of stearic acid was slowly added to the mixture with vigorous stirring for 6 h. Once the reaction was completed, the reaction mixture was cooled, the modified cotton mat was collected, and washed three times with ethanol. The final product was vacuum-dried at 60 °C overnight.

**Characterization.** For the measurement of cellulose content of the raw cotton fiber, the cotton fiber was washed with a 50% NaOH solution and detergent at 100 °C for 2 h and dried under vacuum at 60 °C overnight. The density of cotton fiber samples was measured by Archimedes’ method using isopropyl alcohol solvent at 23 °C. For an accessible OH content of cotton fiber samples, dynamic vapor sorption (DVS) coupled with D2O exchange was applied for a week at 23 °C. The accessible OH groups were quantified based on eq 3

\[
A = \frac{m_d - m_i}{m_i (M_{D2O} - M_H2O)} \times 1000 \text{ (mol/kg)}
\]

where A is the accessible OH group content of the sample, \(m_i\) is the dry mass of the sample before exposing it to D2O vapor (g), \(m_d\) is the dry mass of the sample after the D2O exposure (g), \(M_{D2O}\) is the molar mass of the deuterium (2.014 g/mol), and \(M_H2O\) is the molar mass of hydrogen (1.008 g/mol).

Fourier transform infrared (FT-IR) spectra of cotton fiber samples were collected in the attenuated total reflectance (ATR) absorbance mode of a Thermo Scientific NicoletTM iSTTM 10 FT-IR Spectrometer equipped with a diamond crystal ATR attachment. Spectra were measured in the range of 4000–550 cm⁻¹ with a 4.0 cm⁻¹ resolution and 64 scans for each data point. The XRD patterns of the samples were obtained by a desktop X-ray diffractometer (Rigaku, The Woodlands, TX) using Cu Kα (1.54059 Å) radiation with an X-ray generator operating at 20 kV and 30 mA. Data were collected for a 2θ range of 10.0°–40.0° at an angular resolution of 0.01°/s. The crystallinity index \(I_c\) was determined using eq 4

\[
I_c = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100
\]

where \(I_{(002)}\) is the counter reading for the peak intensity at a 2θ angle close to 22.3° and \(I_{(am)}\) is the amorphous counter reading at a 2θ angle at approximately 20°. All 13C CP/MAS NMR spectra were obtained at 11.4 T using a 600 MHz solid-state NMR spectrometer (Agilent) equipped with a 4 mm HFXY MAS probe. All 35C CP/MAS NMR spectra were obtained using a vendor-supplied sequence (tancpx in VNMRJ, Agilent) with a 3 s recycle delay and 2 ms contact time at a 15 kHz spinning rate and at ambient temperature (~25 °C). The 13C NMR chemical shift was externally calibrated with hexamethylbenzene (HMB) of 17.3 ppm relative to tetramethylsilane of 0 ppm. Thermogravimetric analysis (TGA) was carried out by using NETZSCH STA 449 F1 analyzer equipped with an alumina cell. Samples were heated at a constant rate of 10 °C/min from 25.0 up to 700 °C, with an airflow of 50 mL/min and nitrogen (protecting gas) flow of 15 mL/min. The initial thermal decomposition temperature (T_d) was recorded when sample heating resulted in weight loss (<0.5%).

**Contact Angle Measurement and Surface Energy.**

The contact angles of liquid (water, ethylene glycol, and diiodomethane) drops on the sample surfaces were measured with a contact angle goniometer (Ramé-hart, Inc., Mountain Lakes, NJ) to calculate their surface free energies. Fibers from each sample were fixed onto a microscope slide using double-sided tape to create a flat fiber surface. Five reproducible measurements were conducted for each sample.

**Sorption Test of Crude Oil.** Sorption capacity of each fiber sample was determined using the American Society for Testing and Materials (ASTM) methods for oil sorption capacity measurement (F716-18). All of the sorption capacity tests were conducted using identical samples of crude oil (West Texas Intermediate). About 50 mL of crude oil was poured into 500 mL of natural seawater (34 ppt salinity) in a 1.0 L beaker at 20 °C and shaken for 1.0 min to obtain a layer of crude oil. Each preweighed cotton fiber mat sample (approximately 1.0 g) was placed onto the surface of the oil and water mixture. After sorption, the sample was left to drip for 5 min and then weighed. The amount of oil that was sorbed by the sample was calculated, and sorbed oil (g)/sample (g) values were determined. Sorption measurements of crude oil were carried out in triplicate for each type of sample to get average and standard deviation values. The oil sorption kinetics for the raw and modified cotton fiber samples were determined by immersing the samples for varying lengths of time and by quantifying the sorbed oil as a function of contact time.

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Author Contributions
This paper was written through contributions of all authors. All authors have given approval to the final version of the paper. Y.S. prepared all samples and characterized them by XRD, FT-IR, TGA, and tested crude oil sorption, K.S.H. conducted SSNMR, and B.W.A. recorded SEM.

Notes
The authors declare no competing financial interest.

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