Crude Oil Sorption by Raw Cotton

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Received: February 23, 2013
Revised: April 20, 2013
Accepted: April 25, 2013
Published: April 25, 2013

Research Note
pubs.acs.org/IECR

ABSTRACT: Since the recent Deepwater Horizon Gulf of Mexico oil spill, the need for environmentally friendly oil sorbents has intensified. This study deals with the sorption of crude oil by raw cotton, a biodegradable sorbent. To our best knowledge, the data related to crude oil sorption by unprocessed raw cotton and correlation with cotton characteristics such as micronaire, fineness, and maturity are unavailable. More importantly, our work quantifies the oil sorption (g/g) of low micronaire (immature) cotton. Results showed at the minimum level, low micronaire raw cotton has 30.5 g/g crude oil sorption capacity. Furthermore, the crude oil sorption capacity of low micronaire cotton was significantly higher than the sorption capacity of high micronaire cotton. Brunauer—Emmett—Teller (BET) surface area and environmental scanning electron microscopy analyses support the correlation between the quality characteristics of raw cotton and its oil sorption capacity. In contrast to synthetic sorbents, raw cotton with its high crude oil sorption capacity and positive environmental footprint make it an ecologically friendly sorbent for oil spill cleanups.

INTRODUCTION

Oil spills have caused significant environmental and ecological problems.1 Effective decontamination and cleanups are necessary after the spill for the protection of environment and human health. Effective sorbent for an oil spill cleanup should have important characteristics such as oleophilicity, hydrophobicity, oil retention capacity, reusability, and biodegradability.2−4 Although there are currently many cleanup technologies, such as in situ burning and the use of chemical dispersants and sorbents (such as booms and skimmers), the development of environmentally friendly sorbents that have less logistic burden in usage and biodegradable are needed. In addition, availability and economic feasibility plays an important role in the selection of a sorbent material for cleanup operation.5,6 For the efficient application of sorbents, data on the sorbent sorption capacity and a good understanding on the basic mechanism behind their sorption capability are needed. Although many researchers have extensively investigated natural fibers (such as kapok, barley straw, and wool),6,7−9 synthetic polymers,10 and cellulose-based materials11−14 as potential sorbents for oil spill cleanup, data on the sorption capability of these sorbents using crude oil have not been reported. In addition, only a few studies have addressed the mechanism of oil uptake by such materials.15 A clear and thorough understanding on the basic mechanisms governing oil uptake in cellulose-based materials, particularly cotton, is unclear and very limited.

In this study, we report the sorption capacity and the mechanism behind the crude oil sorption of low micronaire (immature) cotton. Micronaire of a cotton fiber relates to its fineness and maturity. Fineness represents the linear density of fibers (measured in millitex) and maturity defines the degree of cellulose deposition (cell-wall development).16 The lower the micronaire of a cotton fiber, the lower its maturity, the higher its surface wax content, and the finer the fiber.17 Low micronaire cotton has less use value and is discounted economically. To the best of our knowledge, this study is the first to report the crude oil sorption by raw cotton and also correlates the crude oil uptake capacity with its characteristics such as micronaire, fineness, and maturity. Our result shows that low micronaire cotton, because of its finer structure and wax content, can absorb higher amounts of oil than regular-grade cottons. In addition, the basic mechanism behind the sorption of crude oil by raw cotton was investigated based on Brunauer—Emmett—Teller (BET) surface area and environmental scanning electron microscopy (ESEM) analyses.

EXPERIMENTAL SECTION

Raw cotton fibers used in this study were procured from Kitten Land Company (Slaton, TX). The unprocessed raw cottons used in this study are different from the material used by Choi and Cloud.18 Characterization of cotton samples for fiber characteristics such as micronaire, fineness, and maturity was carried out at Texas Tech University’s Fiber and Biopolymer Research Institute, using cotton quality testing instruments such as the Uster High Volume Instrument (HVI) and the Uster Advanced Fiber Information System (AFIS). Raw crude oil used in this study was obtained from Midland, TX. The characteristics of raw crude oil at 25 ± 1 ℃ and a relative humidity (RH) of 63% ± 2% were as follows: viscosity = 30 cP, density = 0.97 g cm−3, and surface tension = 30.39 mN m−1.

Oil Sorption Testing Method. Oil sorption capacity of raw cotton was measured using a slightly modified method based on the ASTM Standard F726-06 test method for the sorbent performance of adsorbents (see Figure 1).19 Raw cotton (0.5−0.6 g) was placed in a circular stainless steel mesh and immersed in a glass dish filled with 1500 mL of raw crude oil, such that the circular mesh floated freely in the oil. After the sample was positioned, the dish was
covered with the glass plate. The entire system was placed over a shaker table and was shaken at 75 rpm for 15 min to create a dynamic environment. The oil-soaked sorbent in the mesh was removed and drained for a minimum of 10 min. After the removal of excess oil that had adhered to the surface of the sorbent and that was not adsorbed or absorbed, the sample was transferred to a weighing balance and the sample weight was recorded. The experiment was performed in replicate 10 times, and the average value was taken for calculating the sorption capacity. (A video file describing the experimental procedure is provided in the Supporting Information.) The crude oil sorption capacity was calculated as shown in eq 1:

\[
\text{oil sorption capacity} = \frac{(S_\text{a} - S_\text{o})}{S_0}
\]

where \(S_0\) is the initial dry sorbent weight, \(S_\text{a}\) the weight of sorbent with oil at the end of the sorption test, and the quantity \((S_\text{a} - S_\text{o})\) the net oil sorbed. (All weights are measured in grams.)

Two cotton samples were characterized for their BET surface area, using an automated gas sorption analyzer (QuadraSorb SI Surface Area and Pore Size Analyzer, Quantachrome Instruments, Boynton Beach, FL). Our laboratory does not have this instrument; therefore, we were limited, with regard to the number of samples that could be tested. However, the two samples tested represented a good range in their micronaire value and, hence, were chosen for the BET testing. Tested samples were outgassed at 120 °C for 3 h. Adsorption isotherms were obtained using krypton at a temperature of 77.3 K. Literature suggests that krypton is a better adsorbate for the BET characterization of samples with low surface area (such as cotton) and has been found to measure the correct surface area values.\(^{20}\)

Environmental Scanning Electron Microscopy. A field-emission environmental scanning electron microscopy (ESEM) system (Hitachi, Model S-4800), in conjunction with the cryogenic system (Gatan, Model Alto 2500), was used to image the cotton samples with and without oil. The samples were

Figure 1. Crude oil uptake by raw cotton.
coated with platinum/palladium at −130 °C, and ESEM images of the coated sample were captured at −130 °C.

### RESULTS AND DISCUSSION

To investigate the effect of the micronaire of raw cotton and to correlate cotton fiber characteristics with the crude oil sorption capacity, raw cottons over a range of micronaires were tested. (Table 1 lists the micronaire values for the cotton samples that have been tested.) Results show that the crude oil sorption capacity of low-micronaire cotton is highest among the different cotton fibers investigated. Figure 2a shows the oil sorption capacity of raw cotton fibers for a range of micronaire values. Low-micronaire cotton (Micronaire 3.1) showed a sorption capacity of 35.83 g/g, which was significantly higher than the sorption capacity of high-micronaire cotton (Micronaire 4.6), which was 30.5 g/g. An inverse nonlinear relationship was found between micronaire values and oil sorption capacity (see Figure 2a).

We propose a new hypothesis for the oil sorption, which takes into account the absorption within the fiber as an important phenomenon, in addition to adsorption and interfiber capillary

Figure 2. Crude oil sorption by raw cotton fibers. (a) Effect of micronaire on oil sorption capacity (g/g). (Cross bars represent standard error of means, n = 10; the regions denoted by an asterisk (*) represent P < 0.05, and the region marked as “n.s.” denotes data that are not significant.) (b) Oil sorption capacity of raw cotton fibers, relative to the fiber characteristics. (The smaller the fineness value (millitex), the finer the fiber and the higher its oil sorption. Fiber with a fineness of 149 millitex has higher oil sorption capacity, versus 175 millitex fiber. Statistical analysis was performed using one-way analysis of variance with Tukey post-test. Statistical significance in oil sorption is shown between low-micronaire cotton (Micronaire 3.1) and other cottons (Micronaire 4.3−4.6). (Cross bars represent standard error of means, n = 10.) (c) ESEM micrograph of sorption of crude oil by raw cotton fibers via interfiber capillary uptake. (d) ESEM image of crude oil absorbed within the fiber showing swelling of the cotton fiber.
distribution.\textsuperscript{4,15} The oil sorption is basically the uptake of oil by the cotton fiber matrix, which involves mechanisms such as adsorption, absorption, and interfiber capillary uptake in the fiber matrix. This hypothesis is supported by the ESEM analysis. Figures 2c and 2d suggest that oil is not only adsorbed on the external surface of the fiber, but also diffused through the fiber matrix via interfiber capillary uptake (see Figure 2c). In addition, because the fibers used are raw, it is well-understood that raw fibers are naturally in twisted form, and once they absorb oil, they swell and become rounded, as is evident from Figure 2d. Thus, the high sorption capacity observed for low-micronaire cotton fibers is due to adsorption, interfiber capillary sorption, and absorption within the fiber, as substantiated by the ESEM images. Furthermore, to comprehend the effect of fiber characteristics such as immaturity and fineness on fiber surface area and oil sorption, BET surface area analysis using krypton was performed. BET surface area values computed using krypton adsorption isotherms for Micronaire 3.1 and Micronaire 4.6 cottons were determined to be 0.665 m\textsuperscript{2} g\textsuperscript{-1} and 0.400 m\textsuperscript{2} g\textsuperscript{-1}, respectively. Since low-micronaire cotton is an immature fiber, it is finer and has a collapsed structure, resulting in a slightly enhanced BET surface area, compared to that of high-micronaire cotton. Enhanced fineness, increased surface area, and less cellulose deposition due to immaturity in low-micronaire cotton result in higher oil sorption. The smaller the fineness of the fiber and lower its maturity (see Table 2), the higher is the oil sorption capacity, as shown in Figure 2b. Results indicate that, in low-micronaire cottons, the combination of higher surface area and increased fineness leads to more sites for surface adsorption and interfiber capillary sorption, which, in turn, results in higher absorption of oil within the fiber than the coarser and more-mature high-micronaire cotton fibers. In addition, swelling of the fiber due to oil absorption within the fiber was also evident, in the case of raw cotton fibers.

Table 1. Micronaire Values of Cotton\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micronaire\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton A</td>
<td>3.1 (0.031)</td>
</tr>
<tr>
<td>Cotton B</td>
<td>3.5 (0.012)</td>
</tr>
<tr>
<td>Cotton C</td>
<td>4.3 (0.021)</td>
</tr>
<tr>
<td>Cotton D</td>
<td>4.4 (0.012)</td>
</tr>
<tr>
<td>Cotton E</td>
<td>4.5 (0.015)</td>
</tr>
<tr>
<td>Cotton F</td>
<td>4.6 (0.016)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Values within parentheses indicate standard deviation. \textsuperscript{b}For the micronaire measurement, the following was observed: one repeat per sample and three samples per cotton type.

Table 2. Properties of Cotton\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fineness\textsuperscript{a}</th>
<th>Maturity Ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton A</td>
<td>149 (2)</td>
<td>84 (1.2)</td>
</tr>
<tr>
<td>Cotton B</td>
<td>154 (4.7)</td>
<td>83 (2.1)</td>
</tr>
<tr>
<td>Cotton C</td>
<td>167 (1.1)</td>
<td>87 (1.2)</td>
</tr>
<tr>
<td>Cotton D</td>
<td>168 (0.6)</td>
<td>89 (0.6)</td>
</tr>
<tr>
<td>Cotton E</td>
<td>173 (0.6)</td>
<td>88 (0.6)</td>
</tr>
<tr>
<td>Cotton F</td>
<td>175 (5.5)</td>
<td>89 (2.5)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Values within parentheses indicate the standard deviation. For the fineness and maturity ratio, the following was observed: one repeat per sample and three samples per cotton type. \textsuperscript{b}The lower the millitex value, the finer the fiber.


