

**Atomic Layer Deposition of Sub-Nanometer Inorganic  
Layers on Natural Cotton to Enhance Oil Sorption  
Performance in Marine Environments**

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## **Abstract**

Over 1 million tons of oil is inadvertently spilled each year. The economic and environmental costs of these spills are enormous and necessitate further development of environmentally friendly sorbent materials. Here, we demonstrate a vapor phase modification approach to create a new class of oil sorbents composed of cellulosic materials (cotton) coated with a sub-nanometer layer of inorganic oxide. This new cellulosic sorbent remains buoyant in water indefinitely and achieves a selective oil sorption capacity ( $23 \text{ g g}^{-1}$  or  $1.05 \text{ g cm}^{-3}$ ) that is at least 35x better than untreated cellulose in aqueous environments. This new sorbent particularly excels under “realistic” conditions like continuous agitation (e.g. simulated waves) and pre-soaking in water (e.g., rain or forced immersion). When sorption performance is compared on a per-volume basis—which better captures use conditions than a per-mass basis—this modified natural product becomes comparable to the best sorbents reported in the literature, most of which require further expensive processing.

## **I. Introduction**

Oil spills continue to be a source of significant ecological damage.<sup>1-3</sup> Improving remediation methods, including oil sorbent technologies, is imperative to further mediate the inherent risks of oil transport necessary in modern society. Methods for oil spill remediation are chosen to balance several concerns, including the physical location of the spill, ecosystem fragility, and economic priorities including oil recovery. For example, while burning and dispersing methods can be effective, they may also exacerbate economic loss or environmental damage.<sup>4</sup> For most open-water spills, skimmers are preferred to recover most of the oil, while sorbents are deployed to remediate portions near the shore or to collect sections that have become dispersed into small droplets.<sup>5</sup>

Sorbent materials collect oil through adsorption and/or absorption processes.<sup>6</sup> Materials that are both hydrophobic and oleophilic with high surface-area-to-volume ratio are ideal oil sorbents for marine environments. Both natural and synthetic materials are used as sorbents. Natural sorbents, like cotton, are inexpensive and can biodegrade if lost, but are often hydrophilic and non-selective for oil sorption. Synthetic sorbents, like polypropylene or polyurethane, are selective oil sorbents but pose a secondary environmental threat if they are not adequately collected following use.<sup>5</sup> After collection, many natural sorbents can be burned productively as fuel, while synthetic sorbents must be shipped to landfills, further contributing to the environmental and economic cost of the spill.<sup>4</sup>

The improvement of sorbent materials is an active area of research, with many groups developing different approaches (as shown in Table I). In general, the goal is to generate porous or “sponge-like” materials with the lowest surface energy possible and the highest bulk surface area/ overall volume ratio. Impressive results have been achieved in the laboratory (with g/g

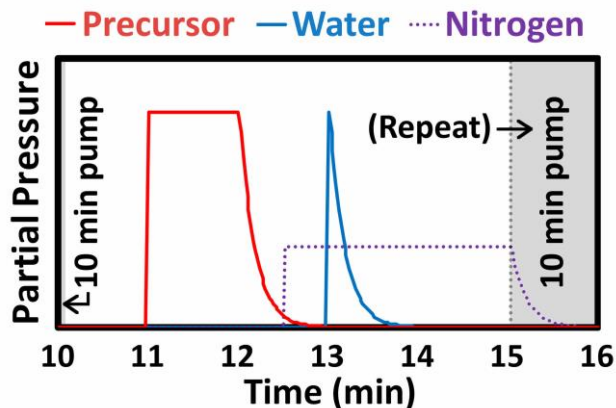
sorption capacities up to 10x higher than that of current commercially available sorbents), but in a 2014 review paper on the subject, Federici and Mintz note there has been little success in commercializing such materials.<sup>5</sup> This is likely due to high costs associated with scaling up production of these materials outside of the lab. Thus, a substantial commercial opportunity exists for a natural, biodegradable material that could be cheaply mass-produced and which matches or outperforms current synthetic sorbents.

One approach to improving the performance of natural sorbents is to modify their surface chemistry. Many examples of this approach have been reported in the literature using organic modifiers.<sup>7-12</sup> Herein, we examine a new approach to surface modification that relies on depositing inorganic species using volatile metalorganic precursors commonly employed for chemical vapor deposition (CVD) and atomic layer deposition (ALD). These inorganic precursors, delivered in the gas phase, rapidly and inexpensively transform cellulosic products into hydrophobic / oleophilic materials appropriate for oil sorption applications. We test the fundamental performance of this new sorbent material as well as its performance in simulated real-world conditions and demonstrate that its performance is at least equivalent if not superior to prior technologies.

## **II. Materials and Methods**

Commercial cotton balls (Up & Up Brand from Target) were used as the primary sorbent material. Other cellulosic materials were examined, including those with better-documented purity, from e.g., Fisher Scientific, but no significant differences in performance were observed. A sub-nanometer inorganic “coating” was applied to the cotton via an atomic layer deposition-type

sequence. ALD was conducted in a custom-built hot-wall viscous flow-tube reactor with two gate valves used for gas isolation. All depositions were carried out at 90 °C using the following protocol: (1) pump down chamber for 10 minutes reaching <10 mTorr, (2) isolate the reaction chamber (close off chamber from the rest of the system and maintain vacuum of  $\approx 10$  mTorr) for 1 minute, then dose the metalorganic precursor (e.g., trimethylaluminum (TMA), diethylzinc (DEZ), or titanium tetrachloride (TiCl<sub>4</sub>)) for 1 second and hold this precursor dose in the chamber for 1 minute, (3) evacuate chamber for 30 seconds, then purge the chamber (i.e., flow nitrogen through at  $\approx 2$  Torr) for 30 seconds, and (4) dose H<sub>2</sub>O for 1 second, purge the chamber for 2 minutes, and then repeat steps 1-4 for subsequent layers. **Figure 1** provides a graphical depiction of this sequence. A single cycle for this process takes about 15 min, but in our experience these pump/purge cycles are excessive, and a modified process taking only 1 min engenders a qualitatively similar degree of hydrophobicity in cellulose. Most of the data reported here is for cotton treated with 2 cycles of trimethylaluminum (TMA). We choose this as our “optimal” treatment because (1) we found it most effective in preventing water sorption, and (2) Lee *et al.* reported it as producing the highest water contact angle for TMA-treated cotton.<sup>13</sup> Finally, it is worth noting that these reactions are self-limiting and usually deposit  $\approx 1$  Å of material per cycle, so the layer of oxide deposited for effective transformation of cotton to a water-repellant oil sorbent is well below 1 nm.



**Figure 1.** Schematic depiction of dosing sequence used to deposit inorganic materials in this study. The 10 min pump-down step is abbreviated for clarity.

Commercial canola oil (Kroger Brand) was employed for most sorption testing, although similar performance was observed for mineral oil (Johnson & Johnson Baby Oil) and in limited testing, crude oil. All reported sorption capacities are averages of at least three independent measurements. The general method across different experimental conditions was to compare the mass of the sorbent prior to sorption of liquid to its mass after sorption of liquid, to yield a common measure of sorbent performance, sorption capacity. Sorption capacities represent the ratio of saturated sorbent to original dry mass, and these measurements were made using an analytical scale. In all cases, the sorbent was allowed to drip for 30 seconds prior to the second weighing. When testing in a mixed oil-water environment, the sorbent was weighed before testing ( $m_i$ ), after sorption of oil and water ( $m_{o+w}$ ), and then after a drying step that removed the water ( $m_o$ ). Water was removed by vacuum drying at 60 °C and  $\approx 10$  torr for 16 hours. These conditions minimized oil loss due to “spattering” that occurs when water is removed more rapidly.

Using these mass values, the sorbent's gravimetric sorption capacities for oil ( $S_o$ ) and water ( $S_w$ ) could be independently calculated:

$$S_o = \frac{m_o}{m_i} \quad [\text{eqn. 1}]$$

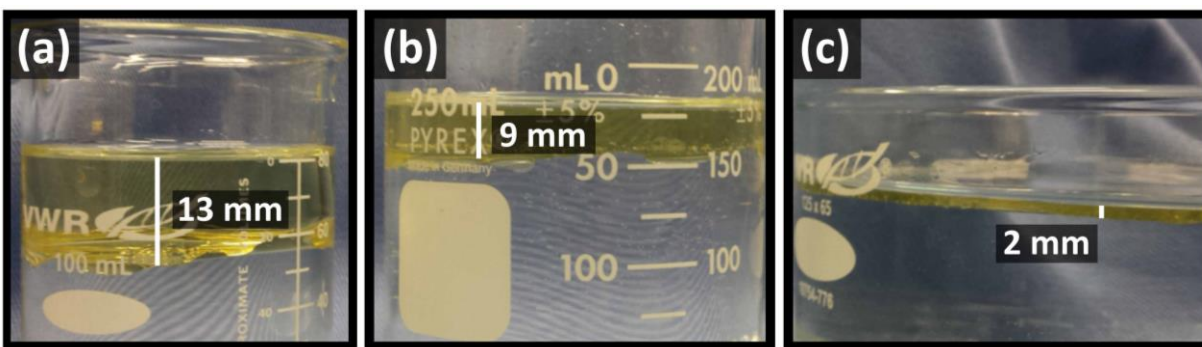
$$S_w = \frac{m_{o+w} - m_o}{m_i} \quad [\text{eqn. 2}]$$

To verify the findings of Parson's et. al. that show hydrophobicity of ALD treated cotton is a maximum at 1-2 cycles, we tested water sorption capacity of ALD treated cotton in pure water over a range of ALD cycle numbers, as shown in **Figure 5**. Oil sorption capacities were also measured over this range to understand the effect of ALD cycle numbers on oil sorption behavior. Because the ALD treated cotton balls float on water, these samples were held underwater during testing to expose their entire surface to water and to more accurately quantify their water sorption capacity. This was accomplished by placing the balls in a fine metal mesh cage which was submerged under DI water in a beaker for the duration of testing. The untreated cotton balls were not forcibly submerged in this way, because they readily sink when placed in water. Similarly, both ALD treated and untreated cotton balls were placed on the surface of the excess oil (>200 mL) used in the pure oil sorption capacity experiments. In both the pure oil and pure water sorption capacity experiments, the cotton balls were weighed before testing, placed in the liquid for 10 minutes, removed and allowed to drip for one minute, then weighed again.

**Figure 8** shows data related to oil sorption for cases that maintain the same oil volume (25 mL) but alter the thickness of the oil layer. This experimental setup was accomplished by using

differently sized beakers: 45 mm diameter, 60 mm diameter, and 125 mm diameter. **Figure 2** shows photographs of these different conditions. The fourth experimental condition, referred to here as “stirred then stopped”, used a 125 mm diameter beaker (2 mm oil layer), in which the oil/water mixture was stirred with a stir bar at  $\approx 400$  rpm for 10 seconds, then allowed to stop spinning for 30 seconds prior to adding the cotton ball. This pre-spinning was done to separate the oil into droplets (to better replicate real-world oil remediation conditions). **Table 1** further describes each condition.

In all four conditions, the cotton balls were weighed before testing, placed on the surface of the oil/water mixture and left to soak for 10 minutes, scooped out and allowed to drip into a waste container for 5 minutes, and weighed again in their saturated (with oil and water) state.



**Figure 2.** Different oil thicknesses corresponding to **Figure 8**. (a) 13 mm thick oil layer in a beaker with an inner diameter of 45 mm. (b) 9 mm thick oil layer in a beaker with an inner diameter of 60 mm. (c) 2 mm thick oil layer in a beaker with an inner diameter of 125 mm.

**Table 1.** Summary of experimental conditions and descriptors used in for experimental conditions used in *Figure 8*.

Condition Descriptor	Condition Description
<b>13 mm thick</b>	13 mm thick layer (25 mL) of oil on excess DI water in beaker with an inner diameter of 45 mm, unperturbed.
<b>9 mm thick</b>	9 mm thick layer (25 mL) of oil on excess DI water in a beaker with an inner diameter of 60 mm, unperturbed.
<b>2 mm thick</b>	2 mm thick layer (25 mL) of oil on excess DI water in beaker with an inner diameter of 125 mm, unperturbed.
<b>Stirred then stopped</b>	25 mL of oil on excess DI water in a beaker with an inner diameter of 125 mm, stirred at a rate of $\approx 400$ RPM via stir bar for 10 seconds to break up the oil into droplets, then unstirred for the duration of the experiment.

**Table 2** describes the set of experimental conditions used to mimic other conditions encountered in real-world oil spill remediation, corresponding to the data reported in **Figure 9**. In each condition, the cotton balls were first weighed, then placed on the surface of the given oil/water mixture and left to sorb for 7 minutes. They were then removed and allowed to drip for one minute prior to weighing. The balls saturated with oil and water were then dried in a vacuum oven at 60° C for 16 hours to remove the water while leaving the oil. Following this treatment, the balls were weighed again, and the mass of oil sorbed was extrapolated from this final measurement.

**Table 2.** Summary of experimental conditions and descriptors used in main text for experimental conditions used in **Figure 9**.

<b>Condition</b>	<b>Description of Measurement Procedures</b>
<b>Wave Agitation</b>	
<b>Standard</b>	25 mL of oil on excess DI water in a beaker with a 150 mm inner diameter on a shaker plate, causing a wave to propagate in a circle about the center of the beaker at a rate of $\approx 120$ RPM.
<b>Pre-Soaked</b>	Identical to “Standard” wave agitation except cotton was submerged under DI water for 5 minutes prior to the experiment.
<b>Mineral Oil</b>	Identical to “Standard” wave agitation except 25 mL of mineral oil was used in place of canola oil.
<b>Stirring</b>	
<b>Stirring</b>	25 mL of oil on excess DI water in a beaker with an inner diameter of 150 mm, stirred at a rate of $\approx 200$ RPM via stir bar for the duration of the experiment.
<b>Salt Water</b>	Identical to “stirring” condition except DI water was replaced with salt water having a composition that simulated that of ocean water.

For “Standard” wave agitation, 25 mL of oil (Kroger brand pure canola oil in one set of trials, Johnson’s Baby Oil mineral oil in another) was added to 450 mL of DI water in beaker with an inner diameter of 150 mm and placed on a VWR Analog Vortex Mixer set to speed “4.5”, which generated a circular wave propagating about the circumference of the beaker at  $\approx 120$  RPM. This

setup effectively emulated environmental wave action, whereby the cellulosic sample was periodically submerged by a wave before resurfacing. The “pre-soaked condition was identical to the “Standard” wave agitation condition; however, the cellulosic samples were submerged underwater for 5 minutes prior to testing. This condition was used to verify that the ALD treated balls retained a high oil sorption capacity even when saturated with water.

In the “stirring” condition, 25 mL of canola oil was added to 600 mL of DI water in a 150 mm diameter beaker with a stir bar added. This beaker was placed on a VWR stir plate set to “1” ( $\approx 200$  rpm) for the duration of the experiment. This condition was an attempt to approximate real-world conditions in which the oil is broken up into small droplets; however, the water vortex caused the oil and cotton ball to migrate to the center of the beaker, where the oil layer was thickest, diminishing the effectiveness of this condition in approximating real-world conditions. For example, the high oil sorption capacity of untreated cellulose in the “salt water” condition is due to this effect, whereby the untreated cellulosic sample was subjected to a thicker layer of oil than it was in the “standard” condition. The “salt water” condition was identical to the “stirring” condition, except rather than DI water, a salt water mixture was created to mimic the composition of sea water. This mixture was made by dissolving the following concentrations of salts into DI water at room temperature, per ASTM D1141-13<sup>14</sup>: 24.53 g/L NaCl, 5.2 g/L MgCl<sub>2</sub>, 4.09 g/L Na<sub>2</sub>SO<sub>4</sub>, and 1.16 g/L CaCl<sub>2</sub>.

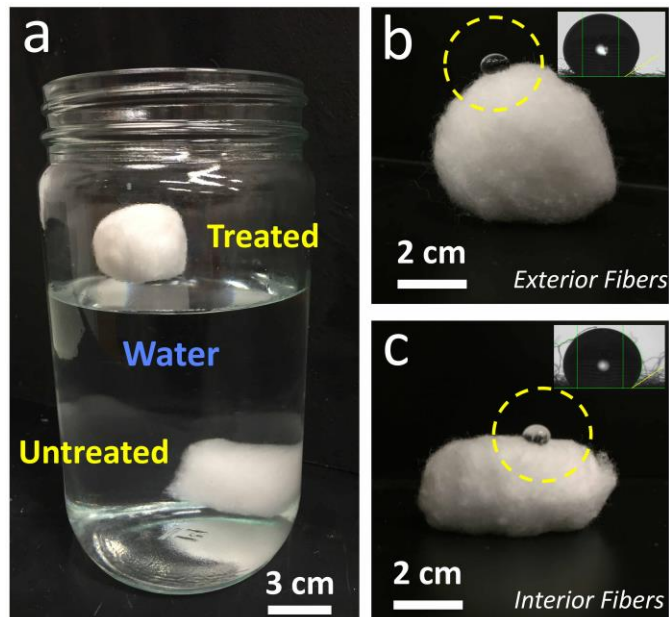
To measure the oil sorption kinetics, cotton sorbents were placed on top of the oil for fixed periods of time, drip-dried for 30 seconds, and weighed. The dripping procedure was consistent with ASTM Standard F726-12<sup>15</sup> and found to be necessary to get reproducible results. Each reported sorption capacity is an average of at least 3 separate experiments (independent cotton balls used in each experiment) with standard errors reported for error bars. Similar protocols were

used for water sorption kinetics except that the cotton was forcibly immersed beneath the water's surface to compel sorption for all cases, including water-repellant ALD-modified sorbents.

### **III. Results and Discussion**

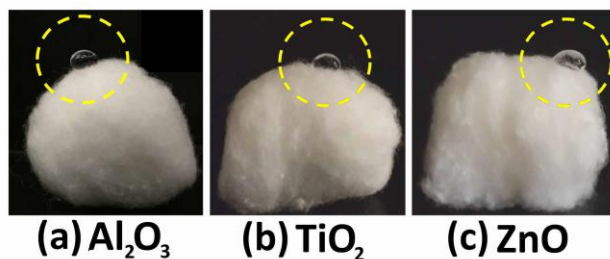
#### **A. General Sorbent Performance of ALD Treated Cotton Material**

In accordance with prior reports<sup>13</sup> we find that 1 to 2 cycles of TMA/H<sub>2</sub>O transforms cotton into a hydrophobic material. **Figure 3a** demonstrates that these treated cotton materials are sufficiently water repellent to be aqueously buoyant. This treatment is surprisingly robust; we have had a similarly treated cotton ball floating in water for over 1 year in our lab. **Figures 3b and c** demonstrate that both exterior and interior fibers exhibit hydrophobic properties. This behavior is consistent with our vapor phase deposition approach. The gaseous precursors readily permeate the entire cotton structure modifying each fiber's surface chemistry, and unlike a liquid-phase modification process, no solvents or post-drying steps are necessary after the chemical modification.



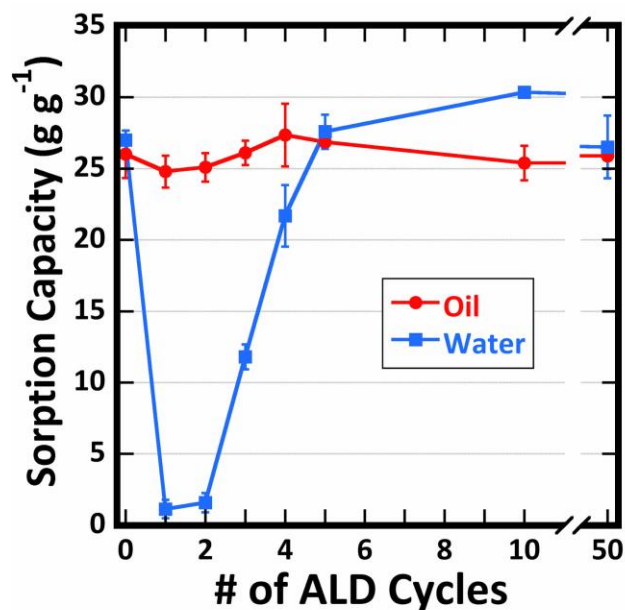
**Figure 3.** (a) Picture of cotton balls dropped in water that are untreated and treated with 2 cycles of TMA ALD. (b) Water beading up on the surface of a cotton ball treated with 2 cycles of TMA ALD. Inset shows image of the water contact angle ( $WCA \approx 153^\circ$ ). (c) A treated cotton ball cut in half, with water beading up on fibers that were previously in the interior of the ball. Inset shows WCA measurement on the interior ( $WCA \approx 146^\circ$ ).

**Figure 4** illustrates that this process is not restricted to only the TMA/H<sub>2</sub>O chemistry. Reactions with other precursors available in our lab, including diethylzinc (DEZ) and titanium tetrachloride (TiCl<sub>4</sub>) have proven equally effective in transforming the cellulose to a hydrophobic material. This flexibility opens up a wide range of possibilities for chemical modification. Currently, the mechanism for this transformation is not entirely understood, but it is believed to be associated with the removal of surface hydroxyl groups and/or the attraction of an adventitious carbon adlayer.<sup>13, 16-19</sup> However, for clarity, this study only focuses on the sorption performance of these materials, not the atomic-scale mechanisms.



**Figure 4.** Photographs of water drops on cotton treated with 2 cycles of 3 different ALD chemistries: (a) Al<sub>2</sub>O<sub>3</sub> using TMA/H<sub>2</sub>O; (b) TiO<sub>2</sub> using TiCl<sub>4</sub>/H<sub>2</sub>O; (c) ZnO using DEZ/H<sub>2</sub>O. Oil sorption data for these different chemistries is given in **Figure 9**.

To evaluate baseline sorption performance, pure oil and pure water sorption capacities were measured (in separate trials) as a function of the number of TMA ALD cycles. **Figure 5** summarizes this data series. After a single TMA/H<sub>2</sub>O dosing sequence the cotton's water sorption capacity drops precipitously (from  $\approx 27 \text{ g g}^{-1}$  to  $\approx 1.1 \text{ g g}^{-1}$ ) while the oil sorption capacity remains mostly unchanged (within error). After two cycles, water sorption capacity remains low, but after three cycles, water sorption capacity begins to increase again. By five TMA/H<sub>2</sub>O cycles, the water sorption capacity is again near the untreated condition. This data suggests that preferential selective sorption of oil over water should be maximized around 1 to 2 TMA/H<sub>2</sub>O cycles. This selectivity is investigated more fully in Section C. Interestingly, if the higher cycle number materials were heated (in any atmosphere) to  $\approx 150^\circ\text{C}$ , hydrophobicity was again induced and selectivity was again possible. Further investigations into this phenomenon are underway.



**Figure 5.** Sorption capacities for cotton with different numbers of TMA ALD cycles in separate trials using pure water and in pure oil.

## B. Water Sorption Kinetics

To better quantify the water repellency of these new materials, we measured the rate of water sorption and fit this data to commonly used kinetics models to extract rate constants. We fit this data to various sorption kinetics models and found the best agreement with the pseudo-second order model first presented by Blanchard and popularized by Ho and McKay.<sup>20-23</sup> This model describes the adsorption rate as:

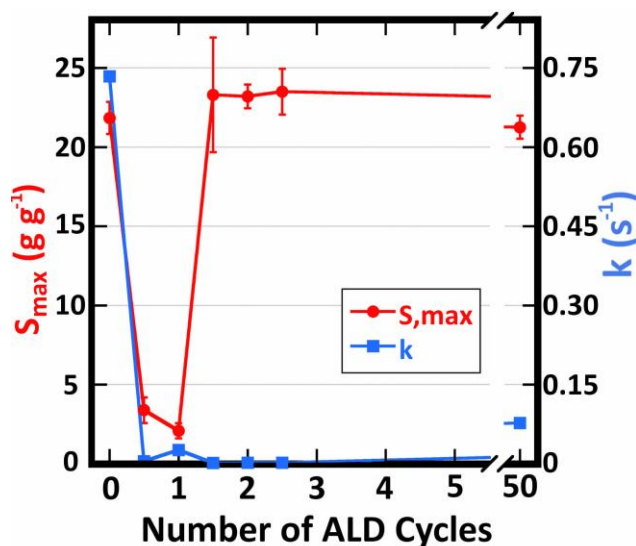
$$\frac{dS_t}{dt} = k(S_{max} - S_t)^2 \quad [\text{eqn. 3}]$$

where  $k$  is the rate constant,  $S_t$  is the sorption capacity ( $\text{g g}^{-1}$ ) at time  $t$ ,  $S_{\text{max}}$  is the maximum sorption capacity ( $\text{g g}^{-1}$ ), and  $t$  is time (s). Integrating eqn. 3 and the applying boundary conditions  $S_t = 0$  at  $t = 0$  and  $S_t = S_t$  at  $t = t$  yields:

$$\frac{t}{S_t} = \frac{1}{k(S_{\text{max}})^2} + \frac{1}{S_{\text{max}}} t \quad [\text{eqn. 4}]$$

We can then linearize our data by plotting  $t/S_t$  versus  $t$  and extract the maximum sorption capacity ( $S_{\text{max}}$ , in  $\text{g g}^{-1}$ ) and rate constant ( $k$ , with units of  $\text{s}^{-1}$ ) for the sorption process using the slope and intercept of the line, respectively. All data sets yield straight lines that closely match the model (with correlation coefficients  $R^2 > 0.98$ ). **Figure 6** summarizes this analysis by plotting the sorbents' maximum sorption capacity and rate constant ( $k$ ) as a function of ALD cycle number. Interestingly, at 3 cycles and beyond, the sorption capacity returns to a value similar to the untreated material ( $\approx 23 \text{ g g}^{-1}$ ), while the sorption rate remains significantly suppressed ( $< 0.05 \text{ s}^{-1}$ ). This result illustrates that all treated cotton sorbents act differently from the untreated material—water sorption rates are significantly slowed.

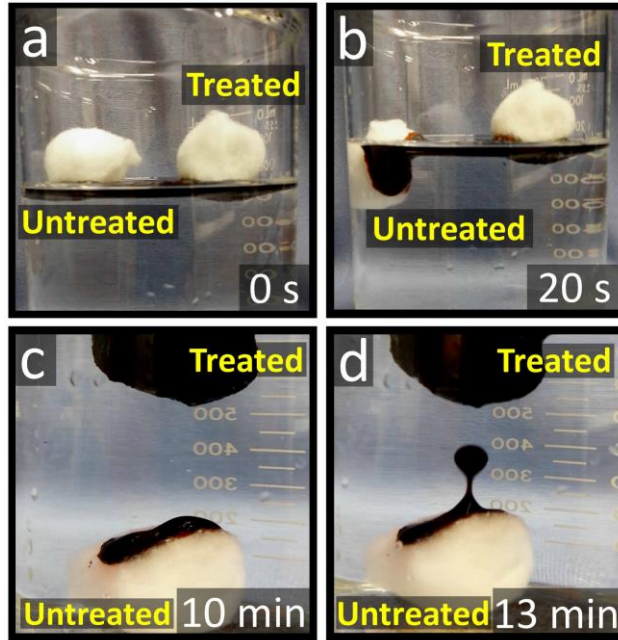
We should also note that these sorption models only provide self-consistent comparisons of sorption kinetics and saturations. Fitting to a given model does not necessarily imply any physical insight about the underlying sorption mechanism. Insight about the mechanism requires more detailed chemical analyses of the process.<sup>24-26</sup>



**Figure 6.** (Red) Maximum water sorption capacities for cotton treated with different numbers of ALD cycles. (Blue) Kinetic rate constant ( $k$ ) for sorption using a pseudo-second order model. All data is for cotton treated with varying number of TMA/H<sub>2</sub>O cycles.

### C. Oil-to-Water Sorption Selectivity

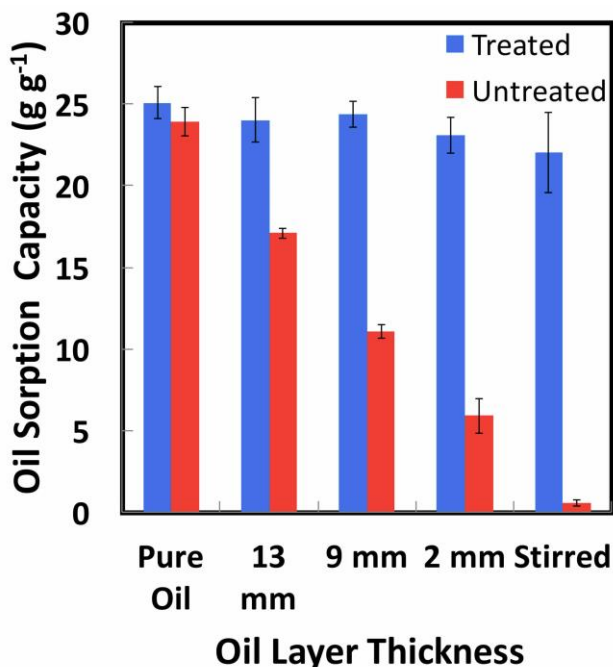
ALD treated cotton sorbents are most impressive in their selectivity for oil sorption in mixed oil and water conditions. While untreated cotton is a good non-selective sorbent for oil, it also readily sorbs water, with its selectivity favoring water sorption. ALD treated cotton has the opposite selectivity, preferring oil sorption. In **Figure 7**, we qualitatively demonstrate this preference in a series of photographs of each sorbent material dropped into an oil-water mixture. As depicted in this photographic time series, untreated cotton quickly sinks through the top oil layer. Once in contact with water it preferentially sorbs the water, while droplets of the previously sorbed oil visibly desorb. When enough of the buoyant oil desorbs, the untreated cotton ball sinks. In contrast, the treated cotton remains indefinitely near the surface sorbing primarily oil.



**Figure 7.** *Photographic time series of untreated and ALD treated cotton immersed in an oil-water mixture: (a) 0 s, (b) 20 s, (c) 10 min, and (d) 13 min after immersion. Oil desorption from the untreated cotton is visible in image (d). The canola oil is dyed brown to improve clarity.*

To further investigate selective oil sorption, we measure the oil sorption capacities for these materials in a series of use cases that maintain the same oil volume (25 mL) but alter the thickness of the oil layer. These conditions were achieved by changing the diameter of the cylindrical container from 45 mm to 125 mm; these different constraints varied the oil layer's thickness from  $\approx 13$  mm to  $\approx 2$  mm. The sorption capacities measured in this set of experiments are plotted in **Figure 8**. While untreated and ALD treated cotton exhibit comparable oil sorption capacity in pure oil, untreated cotton loses sorption capacity when exposed to mixtures of oil and water. As the oil layer's thickness decreases, the untreated cotton more easily sinks through the oil layer and contacts water. Untreated cotton's oil sorption capacity decreases as the oil layer thickness decreases (which results in more contact with water), showing that untreated cotton preferentially

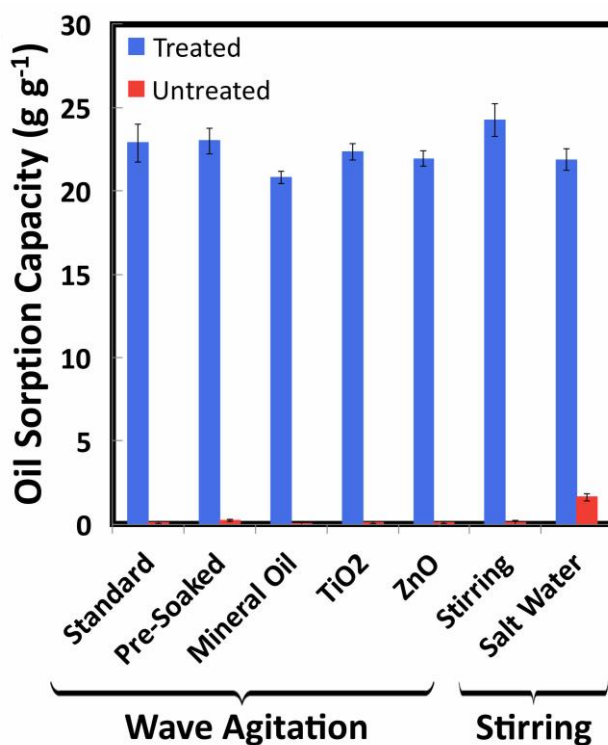
adsorbs water over oil. On the other hand, the ALD treated cotton loses < 10% of its oil sorption capacity as the oil layer thickness decreases. When the oil layer is no longer continuous, the difference in oil sorption capacity between untreated and ALD treated cotton exceeds 35x. This finding is significant because sorbent materials are typically deployed in open water oil spill remediation efforts to compliment skimming to collect more dispersed sections of an oil spill.



**Figure 8.** Oil sorption capacity of cotton treated with 2 cycles of TMA ALD vs. untreated cellulose for a range of different oil thicknesses on DI water.

Next, we consider the oil sorption performance under a variety of modified use cases including active agitation (shaking and stirring), salt water, alternative oils (mineral), and pre-soaking with water. (Additional experimental details are provided in the SI.) Shaking agitation approximates ocean waves. Under these conditions, the untreated cotton ball is observed to immediately sink. In contrast, the ALD treated cotton ball periodically submerges but remains selectively sorbent towards the oil component. As illustrated in **Figure 9**, ALD treated cotton

(including three different precursor chemistries) substantially outperforms the untreated material in all cases and shows nearly equivalent oil sorption performance, within measurement error, for all conditions. A modestly lower sorption capacity for the mineral oil / water mixture can be attributed to the mineral oil's lower density ( $\approx 0.823 \text{ g cm}^{-3}$  versus  $\approx 0.874 \text{ g cm}^{-3}$  for canola oil).<sup>9</sup> Perhaps most interestingly, when we presoak the ALD treated cotton with water prior to use in mixed oil and water with simulated wave conditions, it retains its full oil sorption capacity, (the second condition shown in **Figure 9**). This result suggests that even if this sorbent gets wet, for example, in a rain storm, it will retain high sorbent performance.



**Figure 9.** ALD treated vs. untreated oil sorption capacity across different experimental conditions approximating real-world oil spill conditions.

#### **IV. Conclusions**

Sub-nanometer oxide surface modifications applied to cellulose via an ALD-like process transform this natural sorbent into a hydrophobic material that preferentially sorbs oil over water. One to two ALD cycles are sufficient to drive this transformation and create a cotton material that indefinitely floats on water. Compared to untreated cotton, this ALD treated sorbent shows at least 35x greater oil sorption capacity in simulated use conditions of dispersed oil in water with wave agitation. No loss in this sorption capacity ( $24 \text{ g g}^{-1}$  or  $1.02 \text{ g cm}^{-3}$ ) is observed, even if the ALD treated cotton is first “pre-soaked” with water. This performance, along with the simplicity of synthesis, and potential for retained biodegradability, makes these materials an exciting new sorbent technology for oil spill remediation in marine environments.

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