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# Assessing the performance of wax-based microsorbents for oil remediation

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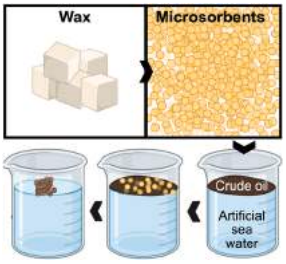
## GRAPHICAL ABSTRACT

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## ABSTRACT

Millions of tons of crude oil are drilled from onshore and offshore locations to satisfy the yearly global fuel demand, increasing the risk for spills and major ecological disasters. Remediation strategies involving chemical surfactants and oil burning are employed, but the toxicity and undesired environmental effects of these treatments raise more concerns and prompt the investigation for alternative approaches. Amongst these novel methods are organic sorbents. In addition to being cost-effective, these materials absorb oil molecules and facilitate oil recovery in an eco-friendly manner. Here, we explore the ability of organic microparticles to improve oil spill clean-up with a focus on interfacial properties and sorption capacities. We investigate the potential of soy, soy-bee and carnauba waxes as secondary oil remediation technology. The waxes are used to design hollow-core microcapsules, which confer them a superoleophilicity ideal for oil recovery. The wax-based microcapsules can remediate oils, including crude oil, mineral oil, and hexadecane, with a sorption capacity up to 5 times their dry mass. Due to low density and high hydrophobicity, the oil-laden microparticles float on top of the water, easing the collection process. Thus, this study lays the foundation for the development of the new class of wax-based microsorbents, exhibiting attractive physical properties in addition of being made of FDA approved plant and animal derivatives. Future studies involving microparticle-assisted bioremediation will provide new insights on how the design of the microparticles could be tailored to fit various ecosystems.

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## 1. Introduction

Rapid industrialization and need for energy have increased the exploitation of oil resources, leading to about 5 million tons of oil production and transportation every year [1]. Accidental oil spills occur during this transportation through tankers and pipelines, which affect the environment. Oil spills have, therefore, become a major threat to the ecosystem, posing lethal effects in fish, mollusks, plants, and birds [2–5]. Oil coverage over large expanses of the water's surface decreases ocean uptake of air due to less air-water contact. This prevents dissolution of essential gases into the water, hence affecting the aquatic ecosystem [6]. The benthic ecosystem is also affected by heavier components in crude oil as they sink to the ocean floor in the form of oil-associated marine snow [7], leading to adverse environmental and economic impacts. Sensitive ecosystems like wetlands, estuaries, mangroves, shorelines, and fisheries are also tremendously affected by oil spills, and the current technologies to address oil spills are more harmful than advantageous to these ecosystems. The cost for oil-spill cleanup is estimated to be $147,000–$294,000/ton of oil [8]. Due to the limitations and high cost of existing cleanup techniques, it is important to develop highly efficient, cheap, and sustainable strategies to remediate if not avoid future spills.

Primary oil spill cleanup strategies can be broadly divided into three major groups: physical methods, chemical methods, and biological methods [9,10]. Choice of the technique depends on the amount and type of oil spill, weather conditions, depth of water column, and physical, biological, and economic characteristics of the location of the spill and time of the year [11]. Physical methods use temporary floating barriers, skimmers, and booms to contain the oil and collect the contaminated water-oil mixtures [9]. However, they often fail to contain the oil under higher pressures or when oil escapes under or over the boom, and skimmers require continuous maintenance to prevent oil build-up [9]. Chemical methods involve the use of dispersants to breakdown the oil slick into smaller droplets that microbes can metabolize. The biological methods employ the pre-existing functionality of naturally occurring oil-eating microorganisms. Although this method is effective, it is time-consuming and its efficiency is dependent on complex interplay among microbes and abiotic parameters like temperature, pH, and nutrient availability [12–14]. Thus, in-situ burning of the oil remain the most effective remediation technique, as the process can eliminate up to 98% of an oil spill; however, it reduces the local air quality due to the release of combustion byproducts, and is therefore not sustainable. Moreover, the elevated toxicity and acute $LC_{50}$ (lethal concentration 50%) values of the residual and dispersed oil urge for safer measures for handling the aftermaths of these primary remediation techniques [15].

Sorbent technology provides an attractive secondary means to alleviate the long-lasting effects of the spills due to its low cost and high efficiency. Sorbents can be broadly divided into three types: synthetic sorbents (e.g., polypropylene), natural inorganic sorbents (e.g., cotton, milkweed, kapok fibers, vermiculite, fly ash), and natural organic sorbents (e.g., rice husk, sugar cane bagasse) [9,16]. Although highly efficient in absorbing oil, the synthetic sorbents pose a threat to environment because of their low-degradability. In fact, chemically modified synthetic sorbents with improved sorption capacity can release hazardous chemical species with increased bioavailability, posing a more serious threat to the aquatic flora and fauna [17]. On the contrary, the natural organic and inorganic sorbents might not be toxic but lack selectivity or exhibit low oil sorption and retention capacities. The shortcomings are commonly addressed through mechanical, thermal, and chemical modifications [16,18,19]. For instance, grinding can improve oil sorption capacity of sorbents by increasing the binding sites on smaller sorbent particles [20]. However, this mechanical modification is not effective for all sorbents, especially for kapok [20–23]. On the other hand, thermal modification can become expensive and time-consuming, as it requires additional pyrolysis at temperatures comprised between 250 and 800°C [24,25]. Chemical treatments like mercerization, acetylation, and grafting of natural sorbents can improve oil absorption; however, their toxicity still raises some concerns, limiting their applications [26–28]. Hence, there is an opportunity for exploring novel organic sorbents, which exhibit high potential for oil absorption and sustainable downstream handling. In this regard, the wax-derived products are promising because of being made of biological materials, rendering them eco-friendly.

Natural waxes like soy, bee, and carnauba are FDA-approved and used in the food industry as superhydrophobic coating materials, rendering them safe to the aquatic organisms [29,30]. The soy contains phosphorous and nitrogen in the form of lecithin, a phospholipid, and plant-based proteins. In oil-rich regions, phosphorous and nitrogen are often deficient, but critical for biological growth [31]. Thus, we anticipated that the wax-based sorbents could exhibit interesting material properties [32,33]. Due to their hydrophobicity, the microparticles could display high selectivity to oil over water. In this study, we propose to investigate the effectiveness of wax-derived microcapsules as secondary cleanup strategy for oil spills. We evaluated the interfacial properties and selectivity to oils of three microparticles generated with 100% soy, 60% soy and 40% bee (soy-bee), and 100% carnauba waxes. Because these microparticles of biological sources do not present any risk of microplastic pollution, they could serve as an excellent alternative to the synthetic sorbent currently used as a secondary remediation technology.

## 2. Materials and methods

### 2.1. Materials

PRP® (Petroleum Remediation Product) microparticles made of 100% soy, 60% soy and 40% bee (soy-bee), and 100% carnauba waxes are manufactured by United Remediation Technology, LLC (PA, USA). Crude oil was obtained under chain of custody to Dr. David Murphy (University of South Florida) as a source oil from the riser of the *Deepwater Horizon* oil spill. Mineral oil and Petroleum naphtha were obtained from Professor Götz Veser Lab (University of Pittsburgh). Hexadecane was purchased from Thermo-Fisher Scientific, USA. Physical parameters of the oils are listed in the table below.

### 2.2. Size characterization

Microencapsulation technology using spray drying enabled the synthesis of the hollow microparticles [34–36]. The size of the microparticles were characterized by measuring the diameter of the microparticles from the scanning electron microscopy images. Multiple regions of the sample were considered for this analysis; six images were analyzed for each condition. The particle diameter was calculated by using Image J.

### 2.3. Electron microscopy

The surface morphology of microparticles was characterized by scanning electron microscopy (SEM). As-received microparticles were deposited on carbon-film-coated specimen stubs, followed by sputter coating 3 nm of Au-Pd using Denton sputter coater prior to imaging. The sample-loaded specimen stubs were then imaged using Zeiss SIGMA500 VP scanning electron microscope at an accelerating voltage of 1 kV.

### 2.4. Contact angle measurement

Contact angle measurements were performed on the bulk wax surfaces and on individual particles. Wettability of the wax surfaces was analyzed by measuring the contact angle formed by water and oil droplets on the surfaces. Briefly, the contact angle of wax surfaces was measured by placing a 10 μL water or oil droplet on the sample surface. To measure the water contact angle of individual particles, a single

particle was absorbed to a 10 μL water droplet held at the tip of a needle. Similarly, the oil contact angle of individual particles was measured by absorbing a single particle to a 10 μL oil droplet held at the tip of the needle. High resolution images of these measurements were captured using a CCD camera and processed through Image J to analyze the contact angle [37].

### 2.5. Interfacial activity

Interfacial activity of the surface-active components from the microparticles were characterized using pendant drop tensiometry. To extract the surface-active components into the aqueous phase, microparticles were heated (0.2 g/mL) in water to obtain a homogeneous solution. The mixture was subsequently cooled down, and the supernatants were filtered using a 0.45 μm filter to obtain the solution containing surface-active components. Pendant drop tensiometry experiments were performed by exposing a 20 μL hexadecane droplet held at the tip of an inverted needle immersed in the above solution. As the soluble components from the solution absorb to the interfaces, the interfacial tension (IFT) reduces over time. This reduction in IFT was analyzed by measuring the dynamic IFT for a period of 24 h until equilibrium was attained. An image of the droplet was captured using CCD camera, and using the Young-Laplace equation, the IFT was obtained. The aged droplet was compressed by withdrawing the hexadecane from the needle at the rate of 1 μL/sec, and the appearance of wrinkles at the interfaces indicated the formation of an interfacial film.

### 2.6. Oil spill remediation using microsorbents

Oil spill remediation under static condition was simulated by dropping 10 μL crude oil on 7 mL of water filled in a petri dish. Microparticles were applied to these spills at increasing concentrations, keeping the volume of crude oil constant. Digital and microscopic images of the microsorbents were recorded to capture their sorption behaviors. To evaluate the remediation ability of the microsorbents under agitation, 50 μL crude oil was deposited on 20 mL of artificial seawater in a glass vial. Increasing mass of microsorbents were applied to these spills while keeping the volume of crude oil constant. The suspension was then agitated using a rugged rotator at 70 rpm for a period of 5 min. The amount of oil absorbed was qualitatively assessed using images captured immediately after oil sorption.

### 2.7. Oil sorption capacity

The sorbent particles were weighed in 3.54 × 2.75-inch teabags, followed by exposure to respective oils. To measure the oil absorbed, the tea bags were taken out and equilibrated for 1 min to drain the excess oil before recording the mass using an analytical balance. The amount of oil uptaken was measured at different time points. Measurements were recorded following the above procedure and oil sorption capacity of the sorbents was calculated using:

$$Adsorption \quad ratio \quad \left(\frac{g}{g}\right) = \frac{(W_f - W_{tb}) - W_e}{W_{tb} - W_t},$$

where, $W_f$ is the total weight of teabag loaded with oil and particles, $W_{tb}$ is weight of teabag loaded with particles, $W_e$ is the weight of oil absorbed by empty teabag, and $W_t$ is the weight of empty teabag. All the oil sorption studies were performed in triplicates at room temperature.

### 2.8. Recycling of the microsorbents

The microsorbents were tested for the ability to absorb oil following a desorption process. Desorption experiments were performed by rinsing the oil-microparticle agglomerates with the solvent, petroleum naphtha. These oil-stripped microsorbents were collected by passing the suspension through a steel mesh. Subsequently, the microsorbents were dried and imaged using Zeiss SIGMA500 VP scanning electron microscope to observe the changes in surface morphology. Second cycle of oil absorption was performed, and the oil sorption capacity of the oil-stripped microsorbents was assessed as previously described.

## 3. Results and discussion

### 3.1. Surface characterization and wetting behavior of the microsorbents

Polydisperse microparticles generated from 100% soy, 60% soy and 40% bee (soy-bee), and 100% carnauba waxes were investigated for their oil sorption capacity. The surface properties of the microparticles were evaluated with SEM and contact angle analyses (Fig. 1a). Six representative images were analyzed using Image J to obtain the size-distribution of soy (n = 82), soy-bee (n = 77), and carnauba (n = 93) microparticles. The size distribution of the microparticles ranged from 0 to 300 μm. The average size of the soy, soy-bee, and carnauba microparticles were 114.6 ± 42 μm, 120 ± 60 μm, and 128 ± 49 μm in diameter, respectively (Fig. 1b). The surface texture of the microparticles was evaluated at magnifications of 200–3000 × to determine if the differences in the surface roughness could affect the oil sorption capacity. The soy and soy-bee microparticles exhibited rougher surfaces in contrast to the carnauba microparticles, which exhibited a smoother surface (Fig. 1a). The cross-sectional view of the microsorbents present the non-uniform hollow cores and a high surface area to volume ratio favorable to oil uptake. To understand how such changes could affect the wetting properties of the microparticles, contact angle measurements were performed. The wettability of a material is dependent on its surface structure and its composition [38,39]. The ability of liquid to wet a surface and form a contact angle below 90° is characteristic of a good wetting behavior [40]. In case the contact angle is above 90°, the liquid avoids diffusing into the material, making it non-wettable.

In order to characterize the wettability of the microparticles, the contact angles were measured on individual microparticles with hexadecane or water droplet, revealing the hydrophobicity and the superoleophilicity of the microparticles (Fig. 1c). All the three microparticles exhibited a water contact angle higher than 90°(Fig. 1c and d), depicting their hydrophobicity. Specifically, soy, and soy-bee microparticles showed comparable contact angle of 117.7 ± 11.4° and 117.3 ± 5.6°, respectively, in the presence of water ($p = 0.466$). However, the wetting property of water on the carnauba microparticles was 112 ± 3.2°, which was significantly lower than that of the soy-based microparticles ($p < 0.0001$). Interestingly, such variations seemed negligible when it came to the oil sorption capacity. As shown in Fig. 1c, all the microparticles were completely absorbed in hexadecane with no detectable contact angle, suggesting their superoleophilicity. Therefore, these microsorbents exhibit characteristics of an efficient candidate for oil sorption.

### 3.2. Wetting behavior of soy, soy-bee, and carnauba waxes

To understand the correlation between surface properties, membrane porosity, and superoleophilicity, the microsorbents were denatured through heat exposure for 24 h. The heat treatment allowed separating the water-soluble fraction of the wax from its insoluble portion to assess their wetting behaviors. Thus, soy and soy-bee microsorbents were heated at 70 °C, while the carnauba microparticles were melted at 100 °C, which renders the surface morphology of bulk waxes less rough and the membrane cross-sections less porous compared to the microsorbents (Supporting Information, Fig. S1). The dynamic IFT analyses were conducted with supernatants obtained from the molten microsorbents to determine how the water-soluble fraction of the soy, soy-bee, and carnauba adsorbed to hexadecane. Initially, the clean interface between hexadecane and water exhibited an IFT of 53 mN/m (Fig. 2a). However, the IFT dropped drastically upon exposure to the

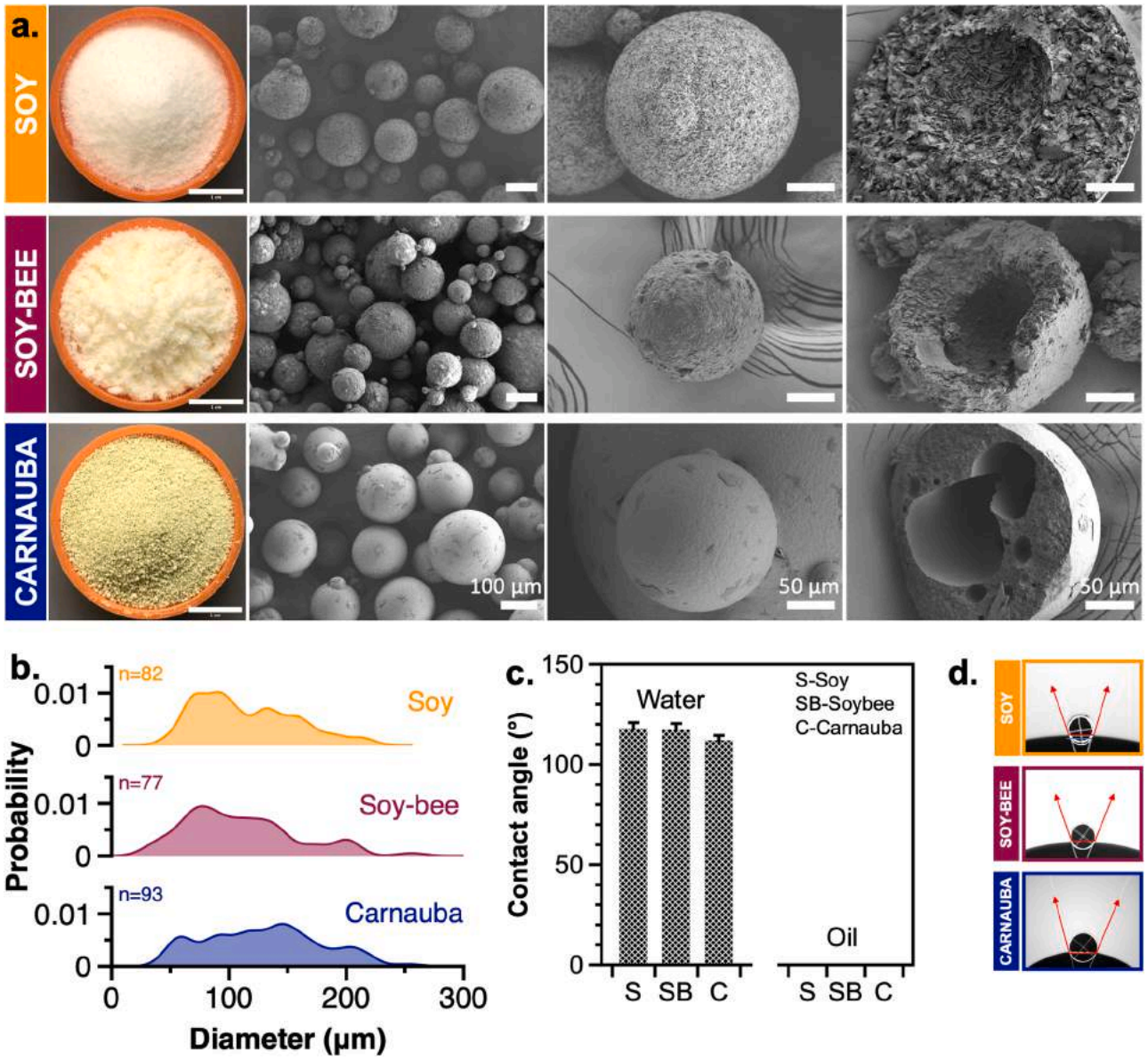


**Fig. 1.** Characterization of wax microparticles. (a) Images showing surface morphology of soy, soy-bee, and carnauba microparticles (Photograph Scale bar = 1 cm). SEM images of soy, soy-bee, and carnauba microparticles at magnification of 200–1000X; (b) size distribution of synthesized soy, soy-bee, and carnauba microparticles; (c) quantitative contact angle measurements of soy, soy-bee, and carnauba microparticles with water and oil; (d) water contact angle images of soy, soy-bee, and carnauba microparticles; three replicates were tested for each condition. Mean and standard deviations are shown.

supernatant solutions, indicating amphiphilic properties from some water-soluble wax components. For all the wax solutions, an equilibrium IFT was achieved in approximately 24 h. The IFT of the soy and soy-bee supernatants were comparable and reached a steady state at around 20 mN/m, while the carnauba supernatant reduced the IFT to a lower equilibrium value, corresponding to 18 mN/m (Fig. 2a, $p < 0.0001$ compared to IFT with pure water). However, the rate of adsorption of soy supernatant was faster than that of soy-bee and carnauba, as indicated by the slopes of the curves. Soy supernatants lowered the IFT at a faster rate of 70.4 mN/m.h compared to soy-bee and carnauba supernatants, which exhibited 38.7 mN/m.h and 50.1 mN/m.h rate of reduction, respectively. The faster absorption of the interface-active molecules released by soy supernatant might suggest their small size.

Similarly, the adsorption of wax molecules to hexadecane was also assessed in the presence of salt using artificial seawater. Our results showed that the presence of salt did not interfere with the adsorption of surface-active agents from the wax supernatants to the oil-water interfaces. In fact, the IFT between hexadecane and all supernatant solutions dropped even further below 14.0 mN/m in the presence of salt (Supporting Information, Fig. S2).

The shape profiles of the aging interfaces formed with the soy, soy-bee, and carnauba supernatants were compared to determine the binding affinity between the soluble wax molecules and interface. The interfaces were compressed after aging for 24 h to allow film desorption or wrinkle formation, which are characteristic of weak or strong binding affinity. (Fig. 2b). Over the course of the interface aging, the hexadecane droplet experienced deformation typical of the drop under IFT due to particle absorption and film formation. However, the compression of droplets at the rate of 1 µL/sec indicated that the three films exhibited different elastic behavior. The appearance of wrinkles upon droplet compression by 70% revealed that only the soy-based solutions spawned paper-like films, which attached to the oil irreversibly [41]. In the contrary, the carnauba supernatant did not present any film; it rather reduced into a spherical droplet upon compression. The lack of

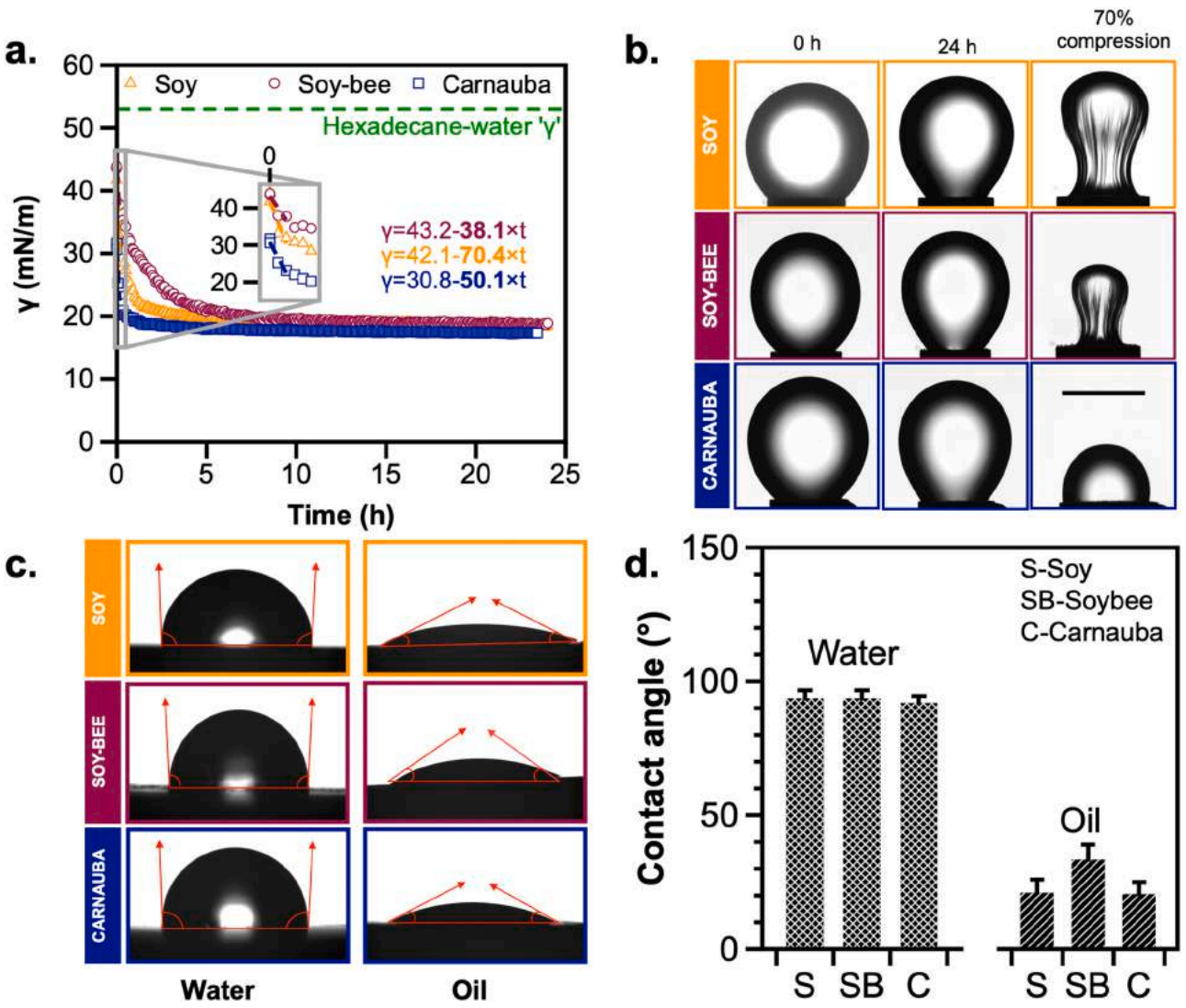


**Fig. 2.** Characterization of wax melts. (a) Dynamic interfacial tension measurements of soy, soy-bee, and carnauba supernatants exposed to hexadecane-water interface plotted against time (t = 0–24 h). The dotted line represents the interfacial tension (53 mN/m) between hexadecane and water. The differences in adsorption rates are presented in the inset. (b) Representative images of the droplet profiles of soy, soy-bee, and carnauba at the beginning of the experiment (t = 0 h), the equilibrium droplet profile (t = 24 h) and the droplets under 70% compression are presented (Scale bar: 1 cm). Interfacial films were observed when the soy and soy-bee supernatant droplets were compressed, but no film was observed on the oil droplet in the presence of carnauba supernatant. (c) Representative contact angle images formed by 10 μL water and hexadecane droplets on soy, soy-bee, and carnauba wax melts are presented. (d) The quantitative analysis of contact angle measurements on soy, soy-bee, and carnauba wax surfaces in the presence of water and oil are shown. Three replicates were tested for each condition. Mean and standard deviations are shown.

interfacial film suggests a weaker interaction followed by the desorption of carnauba-based surfactants from the interfaces [42,43].

The insoluble portions of the wax melts were also assessed for their lipophilic properties. Contact angle analyses revealed that the wax melts were less hydrophobic than the original microsorbents, which was surprising since the hydrophilic fractions of the melts were supposedly removed through heat treatment and were solubilized in the aqueous phase. The soy and the soy-bee wax melts both exhibited a water contact angle of 93.6 ± 3.1° (Fig. 2c and d, $p = 0.172$). The hydrophobicity of the soy-based wax melts was significantly higher than that of carnauba, estimated at 91.9 ± 2.4° (Fig. 2c and d, $p < 0.0001$). More interestingly, the waxes, which were previously found to be superoleophilic (with a hexadecane contact angle of 0°), were now found to be less lipophilic in the melt forms. The hexadecane contact angles were evaluated to 20.5 ± 4.4°, 33.4 ± 5.5°, and 21.0 ± 4.8° for the carnauba, soy-bee, and soy wax melts, respectively (Fig. 2c and d, $p < 0.0001$ compared to microsorbents for all conditions). These results demonstrate that the oleophilic properties of the microsorbents highly depend on their structures, surface chemistry, and roughness. Because the generation of the microsorbents is achieved through homogenization of the waxes in air, the resulting foam-like microsorbents present surface properties and porosity, improving their hydrophobicity and oil sorption capacity. The denaturation of these materials through heat treatment led to the formation of solid and impermeable wax melts, lacking superoleophilicity (Supporting Information, Fig. S1). Therefore, the waxes would appear superior for their oil sorption capacity in their microparticle forms than their molten forms.

### 3.3. Oil sorption capacity of the microsorbents

We anticipated that the hollow structure, porosity, and the surface properties of microsorbents would account for their oil sorption capacity (Fig. 1). To investigate if the hydrophobicity of the three wax materials conferred specific advantages, the microparticles were exposed to crude

oil, mineral oil, and hexadecane, to evaluate their oil absorption rate and the capacity outside of the aqueous environment. Our results in Fig. 3a revealed that the average capacities for crude oil, mineral oil, and hexadecane uptake for soy microsorbents were $4.5 \pm 1.29$ g/g, $4.2 \pm 0.87$ g/g, and $2.4 \pm 0.34$ g/g, respectively. Although the measurements were performed over the span of 48 h, more than 75% of the oil was absorbed in the first hour, and an equilibrium absorption was reached within the remaining period.

The approximate capacities for uptake of crude oil, mineral oil, and hexadecane by soy-bee microsorbents was found to be $4.1 \pm 0.31$ g/g, $3.2 \pm 0.97$ g/g, and $2.8 \pm 0.26$ g/g, respectively (Fig. 3b). The oil absorption was measured over 48 h and showed instantaneous absorption of more than 61% in the first one hour and reached saturation thereafter. Equilibrium absorption was observed after one hour of introduction of microparticles in the oil.

The absorption of crude oil, mineral oil, and hexadecane by carnauba microparticles was found to be $5.1 \pm 0.57$ g/g, $3.3 \pm 0.31$ g/g, and $2.95 \pm 0.53$ g/g, respectively (Fig. 4c). Although the hexadecane absorbed by microparticles was lower than the absorption of crude oil and mineral oil, more than 83% was of the total oil was absorbed in the first one hour of oil sorption. Soy microsorbents recorded significantly higher crude oil absorption compared to hexadecane ($p < 0.0394$). Soy-bee ($p < 0.0129$) and carnauba microparticles ($p < 0.0202$) also showed significantly higher absorption of crude oil compared to hexadecane.

Overall, all the three microsorbents exhibited higher absorption of crude oil compared to hexadecane and mineral oil. The differences in the absorption profile could be attributed to the surface properties, the hydrophobicity, and the porous structure of the microsorbents (Fig. 1). Electron micrographs reveal a major difference in the hollow and porous nature of the microsorbents, which might account for the variations between the oil sorption capacity of the microsorbents (Fig. 1). However, the intrinsic properties of the oils as well as the porosity of the microsorbents might explain the high sorption capacity for crude oil in contrast to mineral oil and hexadecane. Previously, Zhao et al. indicated that high viscosity oil exhibits low liquidity, which could affect their flow within porous materials [44–46]. In our study, crude oil, mineral oil and hexadecane have a viscosity of 12 mPa.s, 32 mPa.s, and 3 mPa.s, respectively (Table 1). However, the density of hexadecane is the lowest. This might explain the high sorption capacity of the microsorbents for crude oil because of its optimal viscosity and density.

To further investigate the performance of the microsorbents in aqueous environments, crude oil from the *Deepwater Horizon* oil spill was used to simulate spills under static condition and agitation. The sorption behavior of the microsorbents revealed that soy (Fig. 4a), soy-bee (Fig. 4b), and carnauba microparticles (Fig. 4c) absorb oil instantaneously. The surface area occupied by freely floating oil was progressively reduced as more microsorbents were introduced in the dish, indicating their excellent oil sorption capacity. The microsorbents coalesced into floating agglomerates, allowing for easy collection. The aggregation of the microsorbents evidenced in Fig. 4 was caused by capillary forces between oil and the microparticles. Also, the Van der Waals force of attraction resulting from the net polarity between the sorbent particles and the oil will account for crude oil retention [10,47]. Such behavior was described in other materials including kapok, cotton, milkweed, and flax fibers, which inherently possess wax coating on their surfaces [10,48–52]. Thus, the surface properties (e.g., hydrophobicity, porosity) and the interfacial forces acting on the microsorbents contribute to the oil absorption behavior [10,53].

Similar results were obtained when the oil absorption studies were performed under high salt concentrations (Supporting Information, Fig. S2–S4) and agitation (Supporting Information, Fig. S5). Although agitation might reduce the residence period of the microsorbents in oil, it would not affect the oil sorption capacity. External forces due to agitation might hinder the oil molecules to enter in contact with the sorbents, and subsequently reduce sorption [54]. We anticipated similar outcome with the use of microsorbents under high agitations in the marine environments. However, the amount of free oil would decrease instantaneously upon more interactions with the microsorbents (Supporting Information Fig. S5). Such phenomena seem to occur regardless of the salt concentration in the aqueous phase. In fact, the effects of salt concentration on oil sorption capacity were assessed in various saline solutions to mimic the aquatic environments experiencing the spills. Our results show no difference in the ability of the microsorbents to absorb oil as the salt concentration was increased (Supporting Information Fig. S2 and S3).

### 3.4. Recycling the microparticles

To assess any benefit for their reusability, the microsorbents were stripped from the crude oil using a solvent—petroleum naphtha. The soy-bee microsorbents clumped after oil recovery using petroleum naphtha, while soy and carnauba microsorbents retained their structure (Fig. 5a). The SEM images of the recycled microsorbents show that their surface structure was well-maintained after stripping the oil (Fig. 5b). The roughness of the soy microparticles increased after oil-stripping (Fig. 5b). On the other hand, carnauba microsorbents maintained their structure and exhibited dark regions on their surface, typical of a residual amount of oil on the surface (Fig. 5b).

The crude oil absorption capacity of soy, soy-bee, and carnauba microparticles in the first absorption cycle was found to be $3.27 \pm 0.63$ g/g, $3.43 \pm 0.48$ g/g, and $3.82 \pm 1.54$ g/g, respectively. However, the oil sorption capacity of all the microsorbents significantly reduced in the second cycle (Fig. 5**c**), presumably because of their denaturation (Supporting Information, Fig. S5). The efficiency of the soy microsorbents reduced by $50 \pm 3\%$ to a sorption capacity of $1.64 \pm 0.41$ g/g ($p < 0.0105$) and that of the soy-bee microsorbents reduced by $61.8 \pm 5\%$ to reach a new sorption capacity of $1.31 \pm 0.45$ g/g ($p < 0.0026$). Carnauba microsorbents absorbed

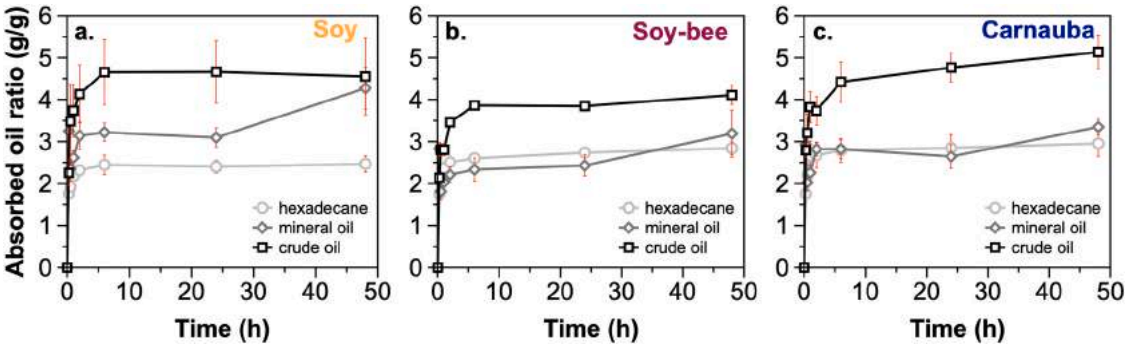


**Fig. 3.** Oil absorption by microparticles. Crude oil, hexadecane and, mineral oil absorption by (a) soy, (b) soy-bee, and (c) carnauba microparticles. Three replicates were tested for each condition. Mean and standard errors are shown.

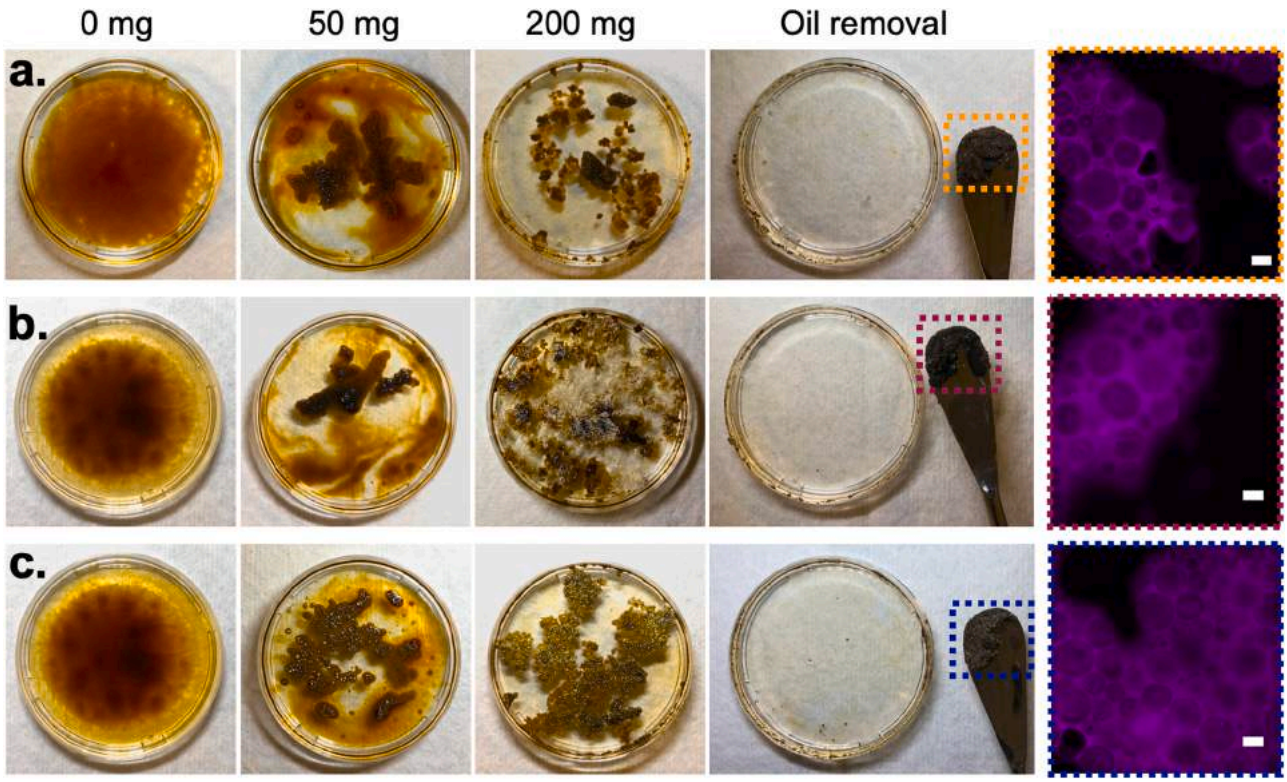


**Fig. 4.** Crude oil absorption by wax microparticles. Oil spill was simulated by depositing 10 μL of crude oil on 7 mL of water in a petri dish (panel 1). Microparticles were added incrementally from 0 (panel 1) to 50 (panel 2) and 200 mg (panel 3). Crude oil absorption by (a) soy, (b) soy-bee; (c) and carnauba microsorbents was evaluated. Panel 4 demonstrates the ease of collecting the oil-laden microparticles after absorption. Panel 5 shows the fluorescent microscopy images of the microsorbents aggregates containing crude oil represented in purple.

**Table 1**
Properties of studied oils at 25 °C.

| | Crude oil | Mineral oil | Hexadecane |
|---|---|---|---|
| Density (g/mL) | 0.840 | 0.876 | 0.7730 |
| Viscosity (mPa.s) | 12 | 32 | 3 |

$1.32 \pm 0.11$ g/g in the second absorption cycle, showing a reduction in efficiency by $65.4 \pm 8\%$ ($p < 0.0247$) compared to the first absorption cycle (Fig. 5c). It is possible that the treatment with petroleum naphtha might alter the surface properties of the microsorbents, which in turn reduce their oil sorption capacity. Previously, it was shown that organic solvents can erode surface coating in cotton fibers [10], which could occur in the microsorbents and reduced their efficiency. Thus, the wax-based microsorbents are not considered a reusable remediation technology. However, their major advantage is their instantaneous oil absorption and high oil retention capacities (Supporting Information Fig. S3), which makes them ideal as secondary remediation technology for sensitive ecological areas such as wetlands, shorelines, mangroves. The degradability in of these materials from biological sources after extended period in oil could be advantageous to sustain the growth of hydrocarbonoclastic microbes in case of accidental release in the environment. Wax microparticles, especially bee wax microparticles, have shown to stimulate microbial population for oil degradation, suggesting that these new class of sorbents could provide unique advantage as eco-friendly technologies [55]. Further optimization of the synthesis of the hollow microsorbents to control their shell thickness and the core

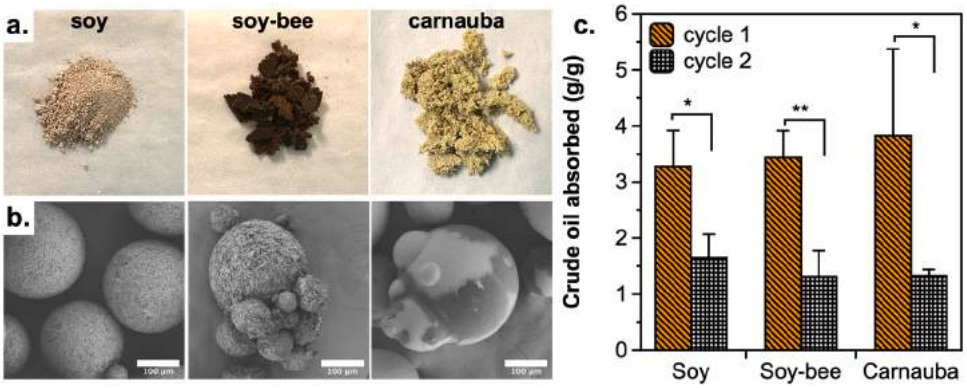


**Fig. 5. Oil desorption and cyclic absorption. (a)** Microparticles after crude oil desorption using petroleum naphtha followed by drying, and (b) corresponding representative SEM images. **(c)** Two cycles of oil absorptions: absorption (cycle 1)—stripping and drying—absorption (cycle 2). Three replicates were tested for each condition. Mean and standard deviations are shown. Scale bar: 100 μm.

size could improve their swelling properties and oil sorption capacity. The synergistic effects of oil sorption and microbial stimulation of the next generation of wax-based microsorbents are part of our on-going work.

## 4. Conclusions and perspective

Microparticles derived from soy, soy-bee and carnauba waxes were investigated for their ability to remediate oil spill. The hydrophobic property of the waxes was enhanced through the synthesis of the porous and hollow core microparticles to confer superoleophilicity. The increased surface-area to volume ratio provided by the microparticles improved the oil sorption capacity of waxes. Thus, soy, soy-bee, and carnauba microparticles instantaneously absorb the oils, with sorption capacities of spanning the range of 2–5 g/g for hexadecane, mineral and crude oils. Upon absorbing the oils, the microsorbents agglomerate and float on the surface of aqueous phase, easing their collection process. Because of their superoleophilicity, the oils remained sequestered in the microsorbents, and this regardless of the salt concentration of the aqueous phase. Our study demonstrate that the oils could be easily stripped from the microparticles using the solvent petroleum naphtha; however, this will alter the surface properties and the sorption capacity of the microcapsules. Thus, the wax-based sorbents appear ideal as a secondary remediation technology to alleviate the long-lasting impacts of oil spills in sensitive eco-systems. The microcapsules' ability to degrade after longer exposure to the oil might suggest that their enclosure in sleeves or cartridge-like containments might minimize secondary pollution through their release in the environment. Conversely, because of being from plant and animal sources, the degradability of the microsorbents in oil might result in biostimulation. Further investigation of the influence of these microsorbents on crude oil bioremediation by indigenous bacteria will reveal if their direct use without containments will make them more suitable for large-scale and rapid treatment of pollution problems caused by oil spills.

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## CRediT authorship contribution statement

**Sricharani R. Balmuri:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Natalie Keck:** Validation, Formal analysis, Investigation, Writing – review & editing. **Tagbo H. R. Niepa:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

## Declaration of Competing Interest

Tagbo H.R. Niepa reports partial financial support for this work was provided by United Remediation Technology, LLC.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2021.127227.

## References

[1] A.A. Al-Majed, A.R. Adebayo, M.E. Hossain, A sustainable approach to controlling oil spills, J. Environ. Manag. 113 (2012) 213–227, https://doi.org/10.1016/j.jenvman.2012.07.034.
[2] S. Moore, R. Dwyer, Effects of oil on marine organisms: a critical assessment of published data, Water Res 8 (10) (1974) 819–827, https://doi.org/10.1016/0043-1354(74)90028-1.
[3] J. Short, Long-term effects of crude oil on developing fish: lessons from the exxon valdez oil spill, Energy Sources 25 (6) (2003) 509–517, https://doi.org/10.1080/00908310390195589.
[4] K.W. Fucik, K.A. Carr, B.J. Balcom, Toxicity of oil and dispersed oil to the eggs and larvae of seven marine fish and invertebrates from the Gulf of Mexico. The Use of Chemicals in Oil Spill Response, ASTM International, 1995, https://doi.org/10.1520/STP15390S.
[5] Ø. Langangen, E. Olsen, L.C. Stige, J. Ohlberger, N.A. Yaragina, F.B. Vikebø, B. Bogstad, N.C. Stenseth, D.Ø. Hjermann, The effects of oil spills on marine fish: Implications of spatial variation in natural mortality, Mar. Pollut. Bull. 119 (1) (2017) 102–109, https://doi.org/10.1016/j.marpolbul.2017.03.037.
[6] A. Whitehead, Interactions between oil-spill pollutants and natural stressors can compound ecotoxicological effects, Integr. Comp. Biol. 53 (4) (2013) 635–647, https://doi.org/10.1093/icb/ict080.
[7] U. Passow, Formation of rapidly-sinking, oil-associated marine snow, Deep Sea Res. Part II Top. Stud. Oceano 129 (2016) 232–240, https://doi.org/10.1016/j.dsr2.2014.10.001.
[8] D.S. Etkin, In Estimating Cleanup Costs For Oil Spills, International Oil Spill Conference, American Petroleum Institute, 1999, pp. 35–39, https://doi.org/10.7901/2169-3358-1999-1-35.
[9] A. Bayat, S.F. Aghamiri, A. Moheb, G.R. Vakili-Nezhaad, Oil spill cleanup from sea water by sorbent materials, Chem. Eng. Technol. Ind. Chem. Equip. Eng. 28 (12) (2005) 1525–1528, https://doi.org/10.1002/ceat.200407083.
[10] H.M. Choi, R.M. Cloud, Natural sorbents in oil spill cleanup, Environ. Sci. Technol. 26 (4) (1992) 772–776, https://doi.org/10.1021/es00028a016.
[11] D. Dave, A.E. Ghaly, Remediation technologies for marine oil spills: a critical review and comparative analysis, Am. J. Environ. Sci. 7 (5) (2011) 423–440, https://doi.org/10.3844/ajessp.2011.423.440.
[12] J. Srivastava, R. Naraian, S. Kalra, H. Chandra, Advances in microbial bioremediation and the factors influencing the process, Int. J. Environ. Sci. Technol. 11 (6) (2014) 1787–1800, https://doi.org/10.1007/s13762-013-0412-z.
[13] S. Sharma, Bioremediation: features, strategies and applications, Asian J. Pharm. Life Sci. 2231 (2012) 4423.
[14] R. Boopathy, Factors limiting bioremediation technologies, Bioresour. Technol. 74 (1) (2000) 63–67, https://doi.org/10.1016/S0960-8524(99)00144-3.
[15] R.C. Prince, Oil spill dispersants: boon or bane? Environ. Sci. Technol. 49 (11) (2015) 6376–6384, https://doi.org/10.1021/acs.est.5b00961.
[16] L. Sobral Hilário, R. Batista dos Anjos, H. Borges de Moraes Juviniano, D. Ribeiro da Silva, Evaluation of thermally treated calotropis procera fiber for the removal of crude oil on the water surface, Materials 12 (23) (2019) 3894, https://doi.org/10.3390/ma12233894.
[17] M. Patel, R. Kumar, K. Kishor, T. Mlsna, C.U. Pittman, D. Mohan, Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods, Chem. Rev. 119 (6) (2019) 3510–3673, https://doi.org/10.1021/acs.chemrev.8b00299.
[18] S. Sidik, A. Jalil, S. Triwahyono, S. Adam, M. Satar, B. Hameed, Modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal, Chem. Eng. J. 203 (2012) 9–18, https://doi.org/10.1016/j.cej.2012.06.132.
[19] R. Asadpour, N.B. Sapari, M.H. Isa, K.U. Orji, Enhancing the hydrophobicity of mangrove bark by esterification for oil adsorption, Water Sci. Technol. 70 (7) (2014) 1220–1228, https://doi.org/10.2166/wst.2014.355.
[20] X. Huang, T.-T. Lim, Performance and mechanism of a hydrophobic–oleophilic kapok filter for oil/water separation, Desalination 190 (1–3) (2006) 295–307, https://doi.org/10.1016/j.desal.2005.09.009.
[21] S. Ibrahim, S. Wang, H.M. Ang, Removal of emulsified oil from oily wastewater using agricultural waste barley straw, Biochem. Eng. J. 49 (1) (2010) 78–83, https://doi.org/10.1016/j.bej.2009.11.013.
[22] H.M. Choi, Needlepunched cotton nonwovens and other natural fibers as oil cleanup sorbents, J. Environ. Sci. Health Part A Environ. Sci. Eng. Toxicol. 31 (6) (1996) 1441–1457, https://doi.org/10.1080/10934529609376434.
[23] M.M. Radetić, D.M. Jocić, P.M. Jovančić, Z.L. Petrović, H.F. Thomas, Recycled wool-based nonwoven material as an oil sorbent, Environ. Sci. Technol. 37 (5) (2003) 1008–1012, https://doi.org/10.1021/es0201303.
[24] I. Uzunov, S. Uzunova, D. Angelova, A. Gigova, Effects of the pyrolysis process on the oil sorption capacity of rice husk, J. Anal. Appl. Pyrolysis 98 (2012) 166–176, https://doi.org/10.1016/j.jaap.2012.07.007.
[25] D. Angelova, I. Uzunov, S. Uzunova, A. Gigova, L. Minchev, Kinetics of oil and oil products adsorption by carbonized rice husks, Chem. Eng. J. 172 (1) (2011) 306–311, https://doi.org/10.1016/j.cej.2011.05.114.

[26] C. Wong, T. McGowan, S.G. Bajwa, D.S. Bajwa, Impact of fiber treatment on the oil absorption characteristics of plant fibers, BioResources 11 (3) (2016) 6452–6463, https://doi.org/10.15376/biores.11.3.6452-6463.
[27] R. Asadpour, N.B. Sapari, M.H. Isa, S. Kakooei, Acetylation of oil palm empty fruit bunch fiber as an adsorbent for removal of crude oil, Environ. Sci. Pollut. Res. 23 (12) (2016) 11740–11750, https://doi.org/10.1007/s11356-016-6349-2.
[28] M.D. Teli, S.P. Valia, Grafting of butyl acrylate on to banana fibers for improved oil absorption, J. Nat. Fibers 13 (4) (2016) 470–476, https://doi.org/10.1080/15440478.2015.1055034.
[29] T. Shen, S. Fan, Y. Li, G. Xu, W. Fan, Preparation of edible non-wettable coating with soybean wax for repelling liquid foods with little residue, Materials 13 (15) (2020), https://doi.org/10.3390/ma13153308.
[30] W. Wang, K. Lockwood, L.M. Boyd, M.D. Davidson, S. Movafaghi, H. Vahabi, S. R. Khetani, A.K. Kota, Superhydrophobic coatings with edible materials, ACS Appl. Mater. Interfaces 8 (29) (2016) 18664–18668, https://doi.org/10.1021/acsami.6b06958.
[31] M. Nikolopoulou, N. Pasadakis, N. Kalogerakis, Enhanced bioremediation of crude oil utilizing lipophilic fertilizers, Desalination 211 (1–3) (2007) 286–295, https://doi.org/10.1016/j.desal.2006.02.095.
[32] R.A. Mathew, V. Lavanya, S. Rasiga, M. Abraham, Bioremediation of marine oil spill using beeswax, Indian J. Geo Mar. Sci. 48 (08) (2019) 1227–1231, https://doi.org/10.2516/ogst/2020053.
[33] R.A. Mathew, M. Abraham, Bioremediation of diesel oil in marine environment, Oil Gas Sci. Technol. Rev. IFP Energ. Nouv. 75 (2020) 60, https://doi.org/10.2516/ogst/2020053.
[34] R. Sun, Y. Lu, K. Chen, Preparation and characterization of hollow hydroxyapatite microspheres by spray drying method, Mat. Sci. Eng.: C. 29 (4) (2009) 1088–1092, https://doi.org/10.1016/j.msec.2008.08.010.
[35] V. Shabde, K. Hoo, Design and operation of a spray dryer for the manufacture of hollow microparticles, Ind. Eng. Chem. Res. 45 (25) (2006) 8329–8337, https://doi.org/10.1021/ie060025s.
[36] M. Ahlers, V. Krone, A. Walch, Microparticles from biodegradable polymers, Adv. Mater. 4 (3) (1992) 230–234, https://doi.org/10.1002/adma.19920040316.
[37] C.A. Schneider, W.S. Rasband, K.W. Eliceiri, NIH Image to ImageJ: 25 years of image analysis, Nat. Methods 9 (7) (2012) 671–675, https://doi.org/10.1038/nmeth.2089.
[38] Y.-L. Hsieh, Liquid transport in fabric structures, Text. Res. J. 65 (5) (1995) 299–307, https://doi.org/10.1177/004051759506500508.
[39] R. Wang, N. Sakai, A. Fujishima, T. Watanabe, K. Hashimoto, Studies of surface wettability conversion on TiO2 single-crystal surfaces, J. Phys. Chem. B 103 (12) (1999) 2188–2194, https://doi.org/10.1021/jp983386x.
[40] R.N. Wenzel, Resistance of solid surfaces to wetting by water, Ind. Eng. Chem. 28 (8) (1936) 988–994, https://doi.org/10.1021/ie50320a024.
[41] J. Hegemann, S. Knoche, S. Egger, M. Kott, S. Demand, A. Unverfehrt, H. Rehage, J. Kierfeld, Pendant capsule elastometry, J. Colloid Interface Sci. 513 (2018) 549–565, https://doi.org/10.1016/j.jcis.2017.11.048.
[42] G. Subbiahdoss, E. Reimhult, Biofilm formation at oil-water interfaces is not a simple function of bacterial hydrophobicity, Colloids Surf. B Biointerfaces 194 (2020), 111163, https://doi.org/10.1016/j.colsurfb.2020.111163.
[43] S.R. Balmuri, N.G. Waters, J. Hegemann, J. Kierfeld, T.H. Niepa, Material properties of interfacial films of mucoid and nonmucoid Pseudomonas aeruginosa isolates, Acta Biomater. 118 (2020) 129–140, https://doi.org/10.1016/j.actbio.2020.10.010.
[44] J. Wu, N. Wang, Y. Zhao, L. Jiang, Simple synthesis of smart magnetically driven fibrous films for remote controllable oil removal, Nanoscale 7 (6) (2015) 2625–2632, https://doi.org/10.1039/C4NR05721J.
[45] Y. Zhao, X. Miao, J. Lin, X. Li, F. Bian, J. Wang, B. Yue, A hierarchical and gradient structured supersorbent comprising three-dimensional interconnected porous fibers for efficient oil spillage cleanup, J. Mater. Chem. 4 (24) (2016) 9635–9643, https://doi.org/10.1039/C6TA02979E.
[46] T.-T. Lim, X. Huang, Evaluation of kapok (Ceiba pentandra (L.) Gaertn.) as a natural hollow hydrophobic–oleophilic fibrous sorbent for oil spill cleanup, Chemosphere 66 (5) (2007) 955–963, https://doi.org/10.1016/j.chemosphere.2006.05.062.
[47] A.A. Hakami, Evaluation of Natural and Synthetic Sorbents for Oil Spill Clean-up Applications. University of Waterloo, 2020.
[48] C.S. Quek, N. Ngadi, M.A. Ahmad Zaini, The oil-absorbing properties of kapok fibre–a commentary, J. Taibah Univ. Sci. 14 (1) (2020) 507–512, https://doi.org/10.1080/16583655.2020.1747767.
[49] I. White, In Oil spill response-Experience, trends, and challenges, paper presented at the SPILLCON, 8th International oil spill Conference, 2010; pp 15–17.
[50] H.-M. Choi, H.-J. Kwon, J.P. Moreau, Cotton nonwovens as oil spill cleanup sorbents, Text. Res. J. 63 (4) (1993) 211–218, https://doi.org/10.1177/004051759306300404.
[51] C.P. Karan, R. Rengasamy, D. Das, Oil spill cleanup by structured fibre assembly, Indian J. Fibre Text. Res. 36 (2011) 190–200.
[52] G. Deschamps, H. Caruel, M.-E. Borredon, C. Bonnin, C. Vignoles, Oil removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents, Environ. Sci. Technol. 37 (5) (2003) 1013–1015, https://doi.org/10.1021/es020061s.
[53] H.-M. Choi, J.P. Moreau, Oil sorption behavior of various sorbents studied by sorption capacity measurement and environmental scanning electron microscopy, Microsc. Res. Tech. 25 (5–6) (1993) 447–455, https://doi.org/10.1002/jemt.1070250516.
[54] J. Zou, X. Liu, W. Chai, X. Zhang, B. Li, Y. Wang, Y. Ma, Sorption of oil from simulated seawater by fatty acid-modified pomelo peel, Desalin. Water Treat. 56 (4) (2015) 939–946, https://doi.org/10.1080/19443994.2014.941302.
[55] B. Waldron, W. Griffin, Evaluation of beeswax based petroleum bioremediation products, WIT Trans. Built Environ. (2002) 62, https://doi.org/10.2495/PORTS020141.