Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1152513

57 (2016) 25591–25599
November

Taylor & Francis
Taylor & Francis Group

Biotemplated *Luffa cylindrica* for the oil spill clean-up from seawater

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Received 15 December 2015; Accepted 5 February 2016

ABSTRACT

Biotemplated *Luffa cylindrica* (B-LC) is used to remove oil spills from Mediterranean seawater. The main objective of this work is to develop a biotemplated organic sorbent. *L. cylindrica* is coated with chitosan for efficient delivery of oil droplets throughout the lumens of fiber. Thus, *L. cylindrica* acted both as a natural sorbent and a chitosan carrier template. In second step, the optimum conditions for the efficient oil sorption of B-LC are determined. Besides seawater tests, DDI water tests are also performed in order to investigate the effect of background water chemistry. Both modified and raw *L. cylindrica* samples are studied for the determination of baseline sorption capacity. SEM and Fourier transform infrared spectroscopy analyses are performed for the characterization studies. Results showed that B-LC has a higher sorption capacity compared to the raw samples. It is understood that increasing temperature has an adverse effect on seawater oil sorption value. It is generally noticed that positive effect of increased contact time and agitation speed is hindered by the increasing temperature values. Effect of background water chemistry is negligible. A slight increase in sorption capacity for the B-LC in seawater is observed. Overall results suggested that the B-LC can effectively be used as an efficient natural sorbent in the oil spill clean-up process.

Keywords: Biotemplate; Chitosan; *Luffa cylindrica*; Oil spill; Seawater; Sorption

1. Introduction

Crude oil, which is crucial for modern civilization, is heterogeneously distributed throughout the earth. 56.5 million bbl/d of oil traveled via seaborne trade which means that about 63% of the world's total oil production moves on maritime routes [1]. Also, a significant amount of oil is drilled from offshore oil platforms. However, catastrophic accidents, which are serious threats on fragile ecosystems, are still remaining as a bottleneck for maritime oil operations. Deepwater Horizon oil spill in April 2010 is considered as the one of the largest accidental marine oil spill in the history. The total estimated volume of leaked oil is 4.9 million barrels, approximately [2]. Clean-up procedures are conducted immediately even conflicts also come into question during the usage of some various chemical agents used up in the cleaning process. Moreover, smaller oil spills from shipping activities are still common. There is also a risk of fuel leaking into the sea during an accident. Also, some ships deliberately release oil into the sea by pumping out oil-laden water below deck while at sea. Although small, these events can still be extremely harmful, particularly when they occur in sensitive marine environments [3]. Coating of oil layer in an aquatic environment may lead to insufficient penetration of

1944-3994/1944-3986

oxygen. Aquatic organisms may be adversely affected by the lack of oxygen and light. Toxic properties of hydrocarbons consist another serious threat on ecosystems. Besides, hydrocarbon-based spills may have detrimental effects on humans via bioaccumulation pathway of marine ecosystems. Moreover, oil spills during drilling and exploration activities on land are also important. Recovery of oil is another aspect that deserves attention in order to prevent economic losses. Therefore, necessity of cheap, easy-to-produce, and biologically degradable oil absorbers is again underlined for the catastrophic oil spill accidents during maritime operations. Electrocoagulation [4], flotation [5], membrane filtration [6], photocatalysis [7], and biological methods [8] are applied in order to solve the current problem. However, significant disadvantages (demulsification and pretreatment necessity, generation of secondary pollutants, high capital and operating costs, membrane fouling, skilled operator necessity, temperature, and pH sensitivity) of these processes make sorption processes more attractive [9]. Sorption with biodegradable materials has considerable advantages over other chemical and biological methods. Such advantages are biodegradable media, superb oil removal efficiency, good recovery potential of oil, fast and easy application procedures, energy efficiency, multiple disposal options, and economical feasibility.

Luffa cylindrica is a tropical plant with fruits possessing a fibrous vascular system. Characteristic microcellular architecture with continuous hollow microchannels (10–20 μm) yields a multimodal hierarchical pore system [10]. Fibrous strands of the *L. cylindrica* network exhibit microspongy structure containing between 200 and 500 microcell fibers leading to high accessible volume and high absorption capacity [11]. Due to their complex and hierarchical pore network, *L. cylindrica* is applied for the removal of cadmium [12], nickel [13], dyes [14], surfactant [15], and oil [16]. Also, applications regarding bioprototyping [17], cell immobilization [18], and composite materials [19] are also studied.

Chitosan is obtained by the deacetylation of chitin and described by its antimicrobial property, cationicity, and film-forming ability. Chitin is a natural biopolymer and exists in the exoskeleton of crustaceans. It is mainly poly(β-(1–4)-2-acetamido-D-glucose), which is structurally identical to cellulose except that a secondary hydroxyl on the second carbon atom of the hexose repeat unit is replaced by an acetamide group [20]. Due to its film-forming ability and affinity for oil chitosan is a proper candidate for the coating of LC in terms of oil sorption goal. Since, inner and outer parts of the LC show different structural properties, only outer parts of the plant are used in order to ensure a homogenous coating procedure. In this study, B-LC material is developed. Besides, oil sorption capacity and effects of environmental parameters (temperature, contact time, and agitation speed) on oil sorption efficiency are also studied in detail.

2. Material and methods

2.1. Preparation of biotemplated L. cylindrica (B-LC)

L. cylindrica samples are gathered from Alanya, Turkey with a subtropical climate. All samples are washed by hot distilled and deionized water to remove residues, and dried subsequently. In order to prepare the 1.0% chitosan solution, 10 g of chitosan (France Chitin) was dispersed in 900 ml of distilled water and 10 ml of acetic acid was added [21]. Alkali treatment and chitosan coating methodology is generally adopted from the previous studies [11,21]. About 2% (w/v) NaOH solution was used for alkali treatment under continuous stirring at 100 rpm and 20°C for 2 h. Then, samples are washed with DDI water and dried at 40°C. Alkali-treated LC samples are immersed into chitosan solution at 300 rpm for 2 h at 60°C. Microcellular and hierarchical architecture of LC provides an ideal medium for the uniform coating of chitosan. Coated samples are dried at 40°C for 24 h. Samples are cut to 5 cm in width into a rectangular prism shape for floating stability in seawater bath tests.

2.2. Oil sorption tests

Commercial motor oil (10W30) is used for oil sorption tests. Sorption tests are conducted in two phases. In the first phase of the study, dry LC and B-LC samples are weighed and soaked only in oil for 5, 10, 15, 20, and 30 min at 20°C without any agitation (oil bath). For the oil bath tests draining is performed by a stainless steel strainer for 1 min till the dropping ends. By the end of this duration, amount of oil is calculated by balance and labeled as ultimate oil sorption (UOS). Oil sorption performance that is called as UOS in this study is measured in terms of sorption capacity (mass of oil sorbed per gram sorbent) by the equation below.

The UOS capacity of samples (W, g/g) was calculated according to the Li et al. [22]:

$$\text{UOS } (W\%) = (G_1 - G_0)/G_0 \times 100 \qquad (1)$$

where G_0 and G_1 represent the weights of the dried sorbent sample and the oil-soaked sample, respectively. UOS capacities of both the samples are determined, accordingly.

Seawater samples were collected from Mediterranean Sea (Antalya, Turkey) and immediately transported to laboratory for the second phase of the study. The collected seawater was filtered by 5- and 1-μm cartridge filters before tests. Table 1 shows the physicochemical characteristics of the filtered seawater samples. A lab-scale spillage simulation is tried to perform with a tank reactor and temperature-controlled shaking water bath. Operating conditions (temperature, contact time, and agitation speed) are varied in order to determine the optimum conditions of oil sorption. Afterward, tank is filled with 600 ml of seawater and 100 ml of oil. Oil sorption capacities of the floating B-LC samples on the seawater surface are determined in seawater bath as seawater oil sorption (SOS). A typical oil spillage cleaning procedure is tried to simulate by the application of various parameters (temperature, contact time, and agitation speed) in tank. Contact time of 5 and 20 min is selected. Agitation speeds of 50 and 130 rpm are applied in order to simulate calm and turbid conditions. Furthermore, two different temperatures are applied. In order to simulate the cold and warm climates, winter average of Danish Straits (6˚C) and summer average of Hormuz Strait, (32˚C) which are both important routes for maritime oil transportation, are selected, respectively. Draining is also performed by a strainer in seawater bath tests. However, since sorbed material is a mix of salty water and oil a simple extraction procedure using hexane is performed according to the standard methods. Amount of oil sorption after this procedure is labeled as SOS.

2.3. FTIR and SEM analyses

The chemical structure and functional groups of the raw and biotemplated samples are tried to identify by Fourier transform infrared spectroscopy (FTIR). For the detection of the samples, the cell was placed in the FTIR scanning path and kept at room temperature. FTIR analyses are performed with KBr pellets. SEM analyses were conducted in a magnitude range of 500–3,000×.

Table 1
Physicochemical characteristics of the filtered seawater samples

Parameter[a]	
pH	8.19
Conductivity (μS/cm) (*T*: 19 C)	57,400
Salinity (‰) (*T*: 19 C)	37.5
Turbidity (NTU)	1.24
Boron (mg/L)	5.1
Nitrate (mg/L)	1.4
Nitrite (mg/L)	0.02

[a]Values are averages of duplicate measurements.

3. Results and discussion

3.1. Impacts of chitosan coating

Before the chitosan coating, an alkali treatment procedure is applied in order to enhance the penetration of chitosan by removing the lignin content of LC [11]. After NaOH treatment, resulting fibers are flat and more capillaries are formed on the surface along the fiber axis that contributes markedly to the retention properties of the material. LC is a superior candidate for oil sorption process in seawater due to its microspongy fibrous system (Fig. 1(a)), which provides efficient transfer of fluids with biodegradable nature as can be seen in SEM images of raw LC in this study. It is generally known that morphology has critical importance in the oil sorption process. LC fibers in the shape of hollow fibers with their empty lumens provide efficient oil entrapment [23]. Moreover, oil layer on the water surface requires a sorbent with good buoyancy for operational simplicity and improved contact between sorbate and sorbent. LC is also an ideal candidate with its good buoyancy property by having very low density (0.02–0.04 g/cm^3). Additionally, chitosan is an environmentally friendly, non-toxic, and biodegradable biopolymer that is even used in food industry [24]. Also, tendency of oil sorption of chitosan is also reported [25]. A synergistic combination of two promising materials is constructed with a bio-inspired coating approach. Thus, a novel and functional material was developed with hierarchical porosity by biotemplating approach (Fig. 1(b)).

Both the materials (LC and B-LC) are tested for their UOS. SEM results proved that significant amount of oil is clearly absorbed by the developed material. Both the B-LC surface (Fig. 1(c)) and capillary (Fig. 1(d)) sections host agglomerated oil droplets. Besides surface section, agglomeration of oil droplets in the capillary sections of B-LC underlines the effective usage of hierarchical pores and efficient delivery of oil through the anastomosis structured lumens. FTIR analyses are also performed in order to evaluate the effect of functional groups on oil sorption both on LC and B-LC. Fig. 2(b) shows the functional groups of 1˚ or 2˚ amines by N–H stretching (3,437 cm^{-1}), alkanes by C–H stretching (2,918 cm^{-1}), carboxylic acid groups by C=O stretching (1,838 cm^{-1}), and C–O

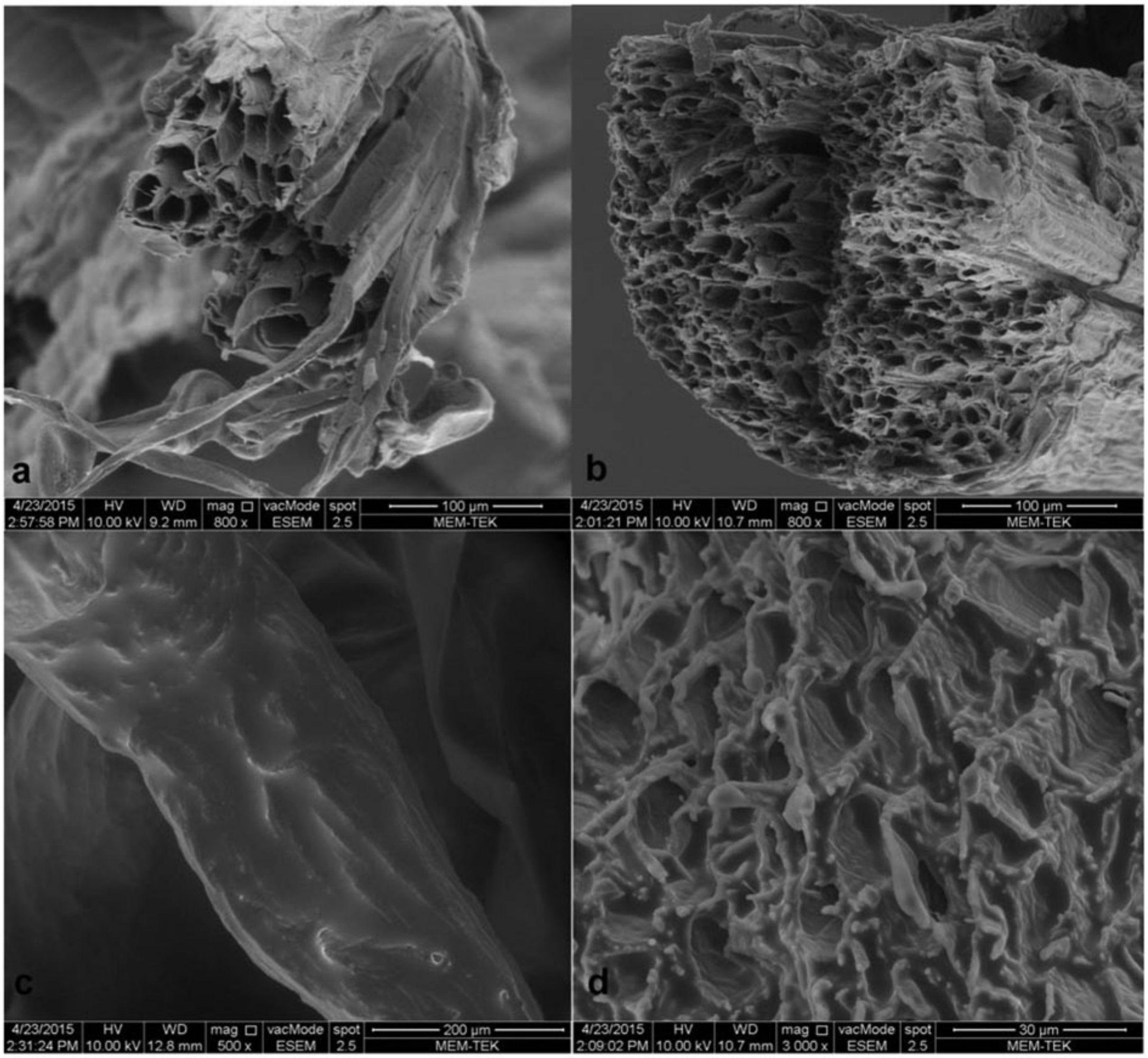

Fig. 1. SEM images of LC and B-LC samples: (a) raw LC sample; (b) raw B-LC sample; (c) surface section of oil soaked B-LC sample; and (d) capillary section of oil soaked B-LC sample.

stretching (1,212 cm^{-1}). It is known that, C=O and C–O groups are responsible from oil adsorption [9]. Besides, Angelova et al. [26], reported that oleophilic alkanes might be responsible for improved oil sorption. It is clearly shown that B-LC gained desired physical and chemical properties by biotemplating according to the FTIR and SEM results.

In the first phase of the study, B-LC and LC samples are tested in order to evaluate the UOS capacity of both the samples. Prepared samples are soaked into 200 ml of oil. Five different contact times (5, 10, 15, 20, and 30 min) are applied in order to determine the optimum contact time for efficient oil sorption. At the end of the contact time samples are drained out in a strainer and weighed. According to the mass balance calculations, UOS capacities of the samples are determined. UOS values are 1.69, 1.51, 1.59, 1.50, and 1.72 g oil/g sorbent for LC and 1.84, 2.08, 2.03, 2.13, and 2.00 g oil/g sorbent for B-LC, respectively (Fig. 3). First phase studies showed that sorption capacity of B-LC was higher than LC for all contact times. UOS capacity was improved between 9 and 42%. This expected behavior proved the effectiveness of biotemplating and affinity of chitosan to oil. Besides sorption process, hindered drainage of oil due to the improved chitosan–oil interaction through-

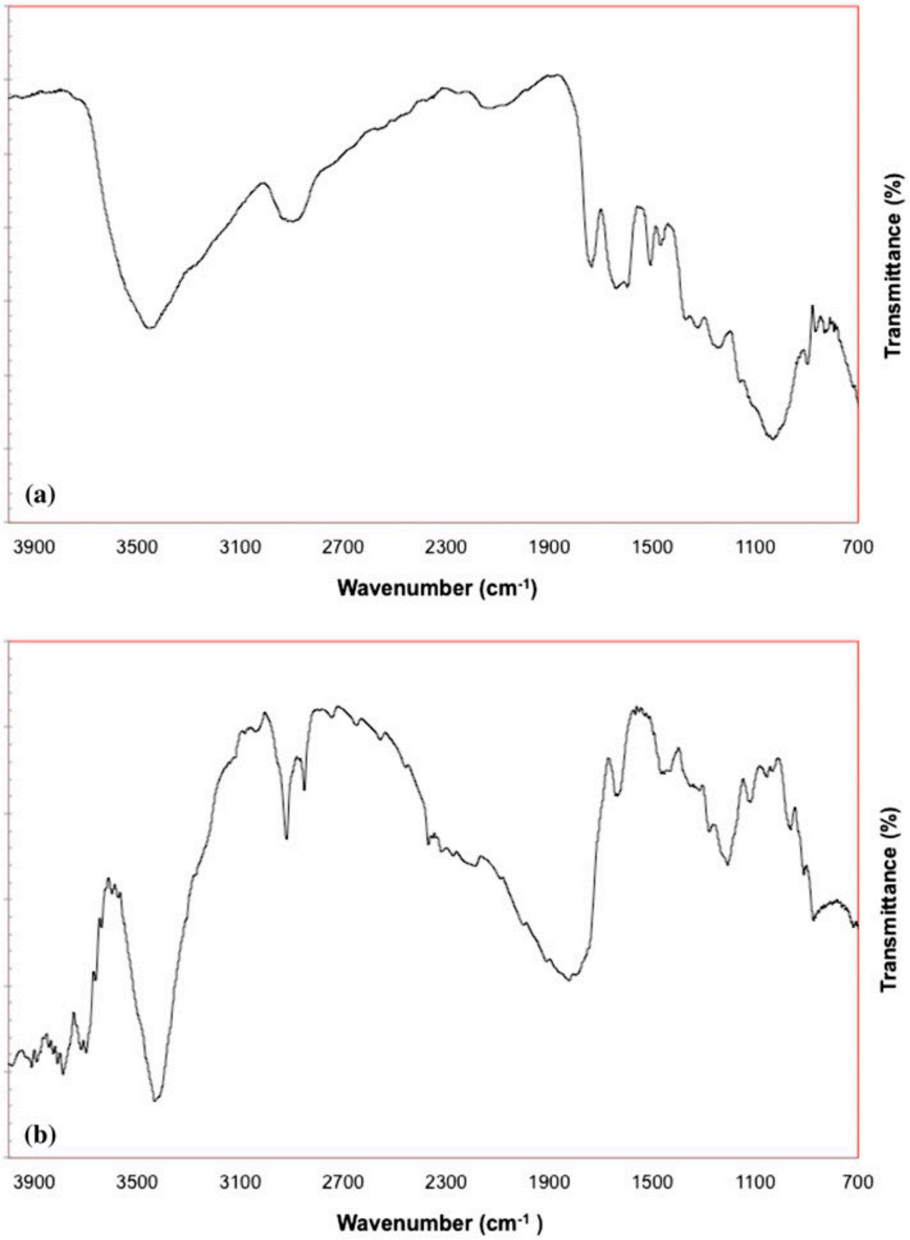

Fig. 2. FTIR spectra of LC (a) and B-LC (b) samples.

out the fiber lumens with better agglomerated oil droplets can be described as other mechanism that enhances oil removal. Thus, the second and third phase studies were conducted only with B-LC. Results showed that maximum oil sorption is obtained for 20 min of contact time (Fig. 3). Minimum oil sorption is obtained for 5-min contact time. However, it is clearly seen from the figure that the oil sorption process is slowed down at 10 min. It is thought that slight increase in oil sorption is negligible for the further contact times. Furthermore, since time is a significantly crucial factor in oil spill clean-up process, contact time of oil sorbent is in critical importance. Because of this reason, both 5 and 20 min of contact times are selected for further experimental phases. The 5 min is selected for the minimum contact time which is necessary for a faster oil spill clean-up process. The 20 min is selected since maximum amount of oil is sorbed throughout the process. The behavior of B-LC at different fluid environments (DDI and seawater), temperature, and agitation speeds are further studied.

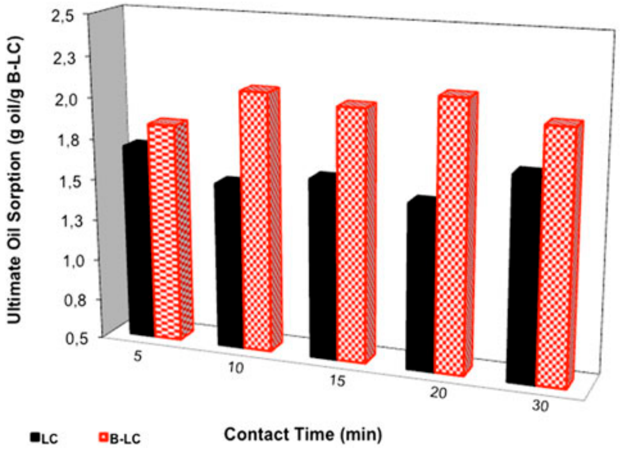

Fig. 3. UOS of LC and B-LC for various contact times (temperature: 20˚C; no agitation).

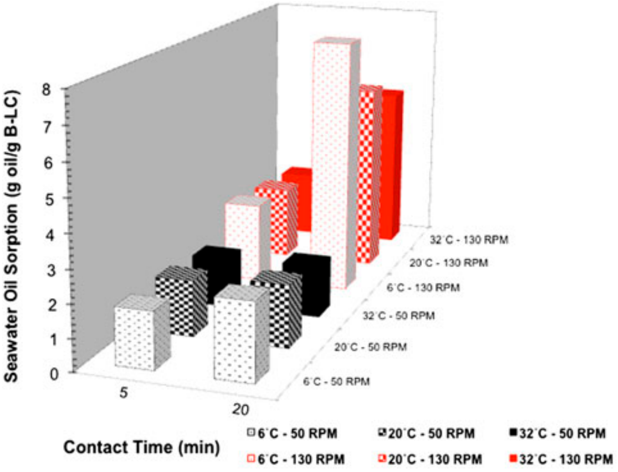

Fig. 4. SOS of B-LC (contact times: 5 and 20 min; agitation speeds: 50 and 130 rpm; temperatures: 6, 20 and 32˚C).

3.2. Impacts of operating conditions

3.2.1. Impacts of temperature

Oil spill clean-up procedures are applied throughout the world in a wide range of climates from cold climate Alaska region (Exxon-Valdez oil spill in 1989) to hot climate Persian Gulf (Gulf War oil spill in 1991). It is well known that, swinging temperature values considerably change oil viscosity. Thus, temperature is selected as an experimental variable. Average seawater temperatures of northern and southern zones of the earth have considerable shifts. Besides 20˚C for the comparison of results with previous phase, summer average of the Persian Gulf (32˚C), and winter average of Danish Strait (6˚C) are selected as the experimental variables. Both the mentioned geographical locations are important maritime routes for international oil transportation. In light of the obtained results, results are generally concordant with the literature, and overall trend is that lower temperatures lead to better oil sorption capacities (Fig. 4). At 50 rpm agitation speed and 5 min of contact time, SOS is decreased by 1.1% for 20˚C and 12.0% for 32˚C in comparison to 6˚C. At 20 min of contact time under same agitation speed, increasing temperature further decreases SOS values. SOS value at 50 rpm agitation speed and 20 min of contact time at 6˚C is 2.38 g oil/g B-LC. This value is decreased by 19.3 and 32.4% for 20 and 32˚C, respectively with corresponding SOS values of 1.92 g oil/g B-LC and 1.61 g oil/g B-LC. This trend is continued in the turbulent conditions at 130 rpm. It is reported that raised temperatures cause lower viscosity that enables accelerated Brownian motion of the sorbate resulted in reduced sorption [27]. Additionally, higher temperature values may lead to increased solubility of oil in water medium that decrease the separation efficiency of oil [23]. It is also thought that improved oil sorption at decreased temperatures may also be linked to the sorbent characteristics besides frequently mentioned viscosity properties of sorbate which is oil in this case. Decreased temperatures may result in narrower capillaries of fiber. Thus, decreased lumen volume enables the entrapment of oil with higher capacities. It is reported that lumens with larger inter-fiber distances that destabilize the liquid bridges between adjacent walls enables greater oil drainage [23]. It should also be noted that drainage of oil during lifting has critical importance on the SOS values. Thus, increased viscosity levels at low temperature may enhance the adherence of oil to sorbent during drainage [28]. Tested oil has approximate viscosity values of 595, 164, and 97 cSt for 6, 20, and 32˚C, respectively. However, it should also be underlined that elevated temperature may increase the chemical interaction of chitosan–oil layer, which can compensate the increased draining affinity of oil from intra fiber pores. It is also reported that more viscous oil may not affect the volume of oil sorption [29]. It should be noted that the decreased SOS values with increasing temperature needs better explanations in the literature and detailed studies of oil absorption are in progress.

3.2.2. Impacts of fluid type and contact time

Fluid type has a slight effect on oil sorption values (Fig. 5). At 50-rpm agitation speed and 5 min of contact time, amount of oil sorption for DDI and SW is 1.55 and 1.73 g oil/g B-LC, respectively where

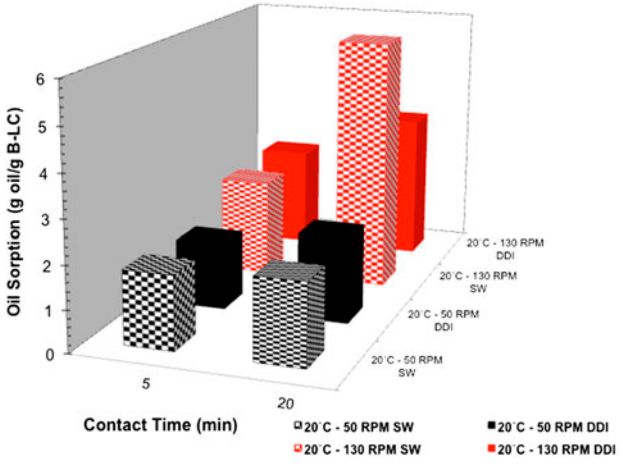

Fig. 5. DDI water and SOS of B-LC at 20˚C (agitation speed: 50 and 130 rpm; fluid type: seawater and DDI; contact time: 5 and 20 min).

2.01- and 1.92-g oil/g B-LC is achieved under same conditions with 20 min of contact time. Significant difference between DDI and SW results at 130 rpm and 20 min of contact time is mainly relying on buoyancy, agitation speed, and contact time, which will be further discussed. These results clearly indicate that effect of background water chemistry (especially salinity) has a negligible effect on oil absorption process. Even results are generally concordant with the literature [30], it should be noted that the effect of salinity on oil absorption process could strongly rely upon oil concentration, presence of ionic substances, and pH.

A sorbent should have enough time to achieve desired sorption values. A minimum time is generally required for the binding of sorbate to the active sites and/or accumulation in the channels, pores, and capillaries. Besides, prolonged contact time enables breakage of oil droplets which further improves the oil sorption efficiency. Thus, enhanced time durations generally improve sorption efficiency. However, extended durations may trigger desorptive effects which decrease ultimate sorption. It is also reported that oil adsorption rate was decreased by increasing contact time [26]. Thus, contact time is in critical importance at the beginning stage of sorption. Near equilibrium, no further significant entrapment happened. Chitosan-targeted studies have reported that significant oil entrapment occurred at 30 min [31]. Besides, efficient oil sorbents should absorb maximum amount of oil in minimum time since there is a “race against time” in order to prevent catastrophic environmental hazards of oil spillage. It seems that a slight increase is observed by the extension of contact time to 20 min at 50 rpm agitation speed. SOS values are increased between 10.9 and 223.0% at prolonged contact times from 5 to 20 min for variable operating parameters (Fig. 4). Furthermore, SOS values are increased by 36, 11, and 5% for 6, 20, and 32˚C, respectively with prolonged contact time. It should be noted that elevated temperatures hinder the SOS increase rate. It can be concluded that increasing SOS values due to the prolonged time is compensated by the increasing temperature. This situation is also observed in the turbulent conditions where SOS values are increased by 223, 161, and 150% for 6, 20, and 32˚C, respectively with prolonged contact time. (Fig. 4). Results suggested that, extended duration of time enables that the oil is transported through the innermost capillary zones of B-LC and find unsaturated zones to be sorbed. Besides, it might be concluded that, even unsaturated zones are absent, agglomeration of oil droplets in the capillaries and surface of B-LC is still ongoing, which is an important aspect for the lifting and drainage stage. It is clearly seen from the figure that prolonged durations consistently improve oil sorption for all agitation speeds and temperatures. This situation is more important at low temperatures where viscosity is high and longer contact times are needed for the saturation of zones [23]. No remarkable change between seawater and DDI water tests for the contact time except at the conditions 130 rpm and 20 min of contact time is observed (Fig. 5). However, buoyancy effect of seawater is higher both for B-LC and oil. Thus, improved buoyancy may create a chance for a better contact of B-LC and oil layer at longer periods of contact. Results obtained at turbulent conditions (130 rpm) strengthen the hypothesis, where floating stability of B-LC is diminished. SOS values are 3.44 g oil/g B-LC and 5.93 g oil/g B-LC for DDI water and seawater, respectively. It is thought that buoyancy of seawater improves the floating stability, and keeping uninterrupted contact of B-LC that resulted in enhanced SOS values.

3.2.3. Impacts of agitation speed

Absorber type cleaners are generally preferred in calm sea surface conditions. However, in some occasions clean-up procedures should be conducted under mild turbulent conditions. Even turbulent conditions are undesirable for clean-up procedure; tight time schedules may force the staff to work in challenging conditions. In order to simulate the calm and turbulent conditions, two agitation speeds are selected. 50 rpm is selected for the calm conditions, while 130 rpm is selected for the turbulent conditions. It is observed that when the agitation speed is increased, absorbed amount of oil is increased as expected. SOS values are increased from 31.2 to 235.2% in turbulent conditions compared to calm conditions under different operating conditions (Fig. 4). This fact can be explained by the breakage and dispersion of the oil droplets which reduce the diameter of droplet (emulsification) that enables more interfacial area for the sorption [31,32]. Besides, enhanced movement of the sorbent may increase the physical contact of deep capillary holes. Synergistic effect of both the mechanisms was resulted in a significant improvement in oil sorption. It should also be noted that, long contact time, both in calm and turbulent conditions (50 and 130 rpm), triggers the penetration of oil into the deep holes of B-LC. At 5 min of contact time, minor changes are observed for the different agitation speeds. However, elevated contact time (20 min) leads to considerable increment in oil sorption at turbulent conditions (130 rpm). This could be explained by the mutualistic interaction of turbulent conditions with prolonged duration of contact time. Positive effect of turbulent conditions on the penetration of oil droplets into the deep capillaries is further stimulated by prolonged duration which may lead to accumulation/agglomeration of oil droplets.

4. Conclusion

A novel, bio-inspired application of chitosan is achieved by the supporting body of *L. cylindrica*. Results showed that the developed B-LC enables improved oil sorption up to 42% by the mechanisms of enhanced oil affinity and improved oil delivery through the lumens of fiber. The effects of operating parameters were also evaluated in terms of fluid type, agitation speed, contact time, and temperature. SOS values are increased from 31.2 to 235.2% in turbulent conditions compared to calm conditions under different operating conditions. Besides, SOS values are increased between 10.9 and 223.0% at prolonged contact times from 5 to 20 min for variable operating parameters. It is understood that increasing temperature has an adverse effect on SOS value. It is generally noticed, that positive effect of increased contact time and agitation speed is hindered by the increasing temperature values. Also, a slight effect of background water chemistry is detected. It is thought that salinity-based buoyancy factor could be a reason. Results overall suggested that biodegradable oil sorbents can be selected for the efficient and fast cleaning of oil spills instead of chemical agents due to their sustainable and biodegradable nature. Also, easy-to-produce natural sorbents provide cost effectiveness and operational simplicity. Therefore, development of a novel, biodegradable, cheap, and easy-to-use absorber may not only provide an optimum solution for oil spill clean-up process, but also may reduce the possible negative impacts of the chemical sorbents on oceans and other water bodies.

Acknowledgments

The author is grateful to Assoc. Prof. Dr Birol Uner for FTIR analyses and Serkan Guclu, MSc for SEM analyses.

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