Crude Oil Removal using *Calotropis procera*

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Calotropis procera (CP) fiber is a natural and renewable material with great lumen and hydrophobic-oleophilic characteristics, providing it with a good oil absorption capacity. In order to increase the absorption efficiency of organic oils and solvents, CP fiber was treated with either 0.1 M NaOH (CPNaOH), 1% $NaClO_2$ ($CPNaClO_2$), or hydrothermal conditions (CPHT) in an effort to improve its ability to remove crude oil from leaks or spills. The fibers were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy with field emission (SEM-FEG), and wettability for water and diesel. The fibers CPHT, CPNaOH, and $CPNaClO_2$ showed excellent hydrophobic-oleophilic properties and good crude oil absorption capacity in water 99.2 g/g, 103.9 g/g, and 92.0 g/g. The absorption after 60 min for most fibers in dry systems or with a layer of oil floating on water exceeded 90% of its absorption capacity for the time of 1440 min. The CPNaOH after 6 runs absorbed 445.8 g of crude oil per gram of fiber. Based on the results, the treated fibers can be considered an alternative for the removal of oil from leaks and spills due to the high availability and excellent absorption property for various oils.

Keywords: Calotropis procera; Absorption; Crude oil

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INTRODUCTION

Crude oil is a natural resource that was formed millions of years ago. When produced, transported, and stored, there is an imminent risk of causing significant impacts (Paul *et al*. 2013). The spillage of oil and its derivatives in water has been a challenge in the world due to the high toxicity and mobility of hydrocarbons. Its presence in the environment may cause continuous contamination by monoaromatic hydrocarbons, aromatic polycyclic hydrocarbons (HPA), and total petroleum hydrocarbons (TPH), as well as generating problems for several years or decades (Rengasamy *et al*. 2011). This is due to the chemical and physical properties of the oil being altered by "weathering," such as evaporation, dissolution, microbial degradation, dispersion, and adsorption in suspended materials and photochemical oxidation (Rengasamy *et al*. 2011; Paul *et al*. 2013; Gros *et al*. 2014; Zengel *et al*. 2016). Therefore, it is important to develop efficient and economically feasible technologies to remove oil hydrocarbons and their derivatives after these accidents (AlAmeri *et al.* 2019).

The mechanical removal of oils in water by sorbent materials can be a very efficient technique (Mysore *et al.* 2005). The characteristics to determine a good oil sorbent include hydrophobicity, oleophillicity, high sorption capacity, fast kinetics of sorption, reuse, and

biodegradability (Prince 2015). The effectiveness of any cleaning technology depends on the individual circumstances of spillage (location, oil type, amount of oil) and also unpredictable variables such as climate (Wahi *et al*. 2014). Among the techniques available for the removal of oil from water, the physical method using sorbents can be one of the most efficient techniques (Pintor *et al*. 2016; van Gelderen *et al*. 2017).

A wide range of sorbent materials has been reported (Wahi *et al.* 2014; Sabir 2015; Pintor *et al*. 2016; van Gelderen *et al*. 2017; Hilário *et al*. 2019), which distribute mainly in three classes: inorganic, synthetic polymers, and natural. Inorganic sorbents are composed of materials such as vermiculite, zeolite, silica, and perlite (Mysore *et al*. 2005; Bastani *et al*. 2006; Zadaka-Amir *et al*. 2013; Yu *et al*. 2017). Their performance is limited by low oil sorption capacity, oil-water selectivity, inadequate buoyancy, and non-biodegradability. Synthetic polymers including materials such as polyurethane sponges, polypropylene fibers, and polystyrene fibers (Ke *et al*. 2014; Renuka *et al*. 2015; Wu *et al*. 2015; Saleem *et al*. 2018) have shown high absorption and recyclability capacity and are commonly marketed for sorption in oil spills due to their high hydrophobicities. These sorbents are efficient; however, they are not biodegradable, which is a great disadvantage. However, the application of organic natural materials derived from plant sources such as rice husk, sawdust, cotton fiber, kapok fiber, and cattail fibers (Adebajo and Frost 2004; Lim and Huang 2007a; Lim and Huang, 2007b; Wang *et al*. 2013a; Wang *et al*. 2013b; Ge *et al*. 2016; Ma *et al*. 2016) have been studied for application in cleaning in oil spills due to their environmentally friendly characteristics, low cost, easy availability, and biodegradability (Ge *et al*. 2016). Hubbe *et al.* (2013) in their review showed that natural cellulose-based fibers can be used as oil sorbents. Encouraging results have been found with similar or even greater capacity to sorb oil from the water surface when compared to typical polypropylene (PP) products that have been used more frequently for this purpose. Moreover, a variety of effective cellulosic materials have been demonstrated for spraying hydrocarbon oils, especially in the absence of water, and their performances in the presence of water can be improved by several pretreatments that make them more hydrophobic (Hubbe *et al*. 2013).

Calotropis procera fiber (CP), from the family Apocynaceae, has a natural wax coating on its surface and lumens (void central space) even larger than the kapok fiber (Thilagavathi *et al*. 2018). CP fiber has oleophilic, hydrophobic characteristics with high sorbent capacity for several oils; it shows greater than 50% re-sorption after 6 reuse cycles (Nascimento *et al.* 2016; Thilagavathi *et al.* 2018; Hilário *et al.* 2019). Thus, it is an excellent alternative for leakage and cleaning an oil spill from the water surface.

To improve the oil sorption properties of natural fibers, they can be modified by (1) chemical treatment, using alkalis/acid, solvent treatment, oxidation treatment, and acetylation (Abdullah *et al*. 2010; Liu and Wang 2011; Liu *et al*. 2012; Wang *et al*. 2012; Wang *et al*. 2013c) and (2) physical treatments such as hydrothermal, radiation, and ultrasonic (Liu *et al*. 2012; Tang *et al*. 2012; Zhang *et al*. 2014). These modifications can be used to develop materials with new hydrophobic-oleophilic characteristics and high oil sorption capabilities (Husseien *et al*. 2008; Razavi *et al*. 2015; Zheng *et al*. 2015; Anuzyte and Vaisis 2018).

The objective of the present work was to modify the fiber with solutions of NaOH, $NaClO_2$, and hydrothermal treatment to alter the surface, surface wax, and hollow structure of the fiber. The effects of treatments on crude oil absorption were evaluated and compared with CP *in natura*. Considering the high performance of CP, its low value, the abundance

of raw materials, and easy synthesis methods, the resulting fibers are promising approaches for cleaning and removing a variety of oils from the water surface.

EXPERIMENTAL

Materials

The *Calotropis procera* (CP) fruits were collected in the municipality of Natal (latitude 5°44'31.00"S and longitude 35°12'18.98"W), Rio Grande do Norte state, Brazil, and the CP fibers were collected and manually separated from the seeds, being dried at room temperature (25 ± 1 °C) for 24 h. For the absorption tests, crude oil (viscosity = 73.6 cP and density at 20 °C = 861.0 kg/m³) classified as medium, º API grade 31.29, and marine diesel (viscosity = 2.789 cP and density at 20 °C = 827.9 kg/m³), was provided by PETROBRAS, Guamaré Pole, Rio Grande do Norte, Brazil. New (viscosity = 62.73 cP and density at 20 °C = 850.0 kg/m³) and used engine lubricant (viscosity = 69.25 cP and density at 20 °C = 854.0 kg/m³) were purchased from the local market, Natal, Rio Grande do Norte state, Brazil. The diesel oil (viscosity = 1.953 cP and density at 20 °C = 813 kg/m³) was acquired from a gas station located in the city of Natal, Rio Grande do Norte, Brazil. Distilled water was produced in the laboratory, while the methyl blue used to dye the distilled water in the selectivity test was acquired from Neon, Suzano, São Paulo, Brazil. The sodium hydroxide Pa ACS (NaOH) was acquired from Vetec, Sigma Aldrich, Duque de Caxias, Rio de Janeiro, Brazil. Sodium chlorite PA ACS ($NaClO_2$) was obtained from Sigma Aldrich Brazil, São Paulo, Brazil. The Benzene PA (viscosity = 0.484 cP and density at 20 °C = 808.0 kg/m³) was acquired from Neon, Suzano, São Paulo, Brazil.

Methods

Fiber treatment

Three processes of treatment of fibers *in natura* were performed. The first consisted of hydrothermal treatment in water (CPHT), with the immersion of 2 g of fiber in 400 mL of heated water at 80 °C with agitation for 1 h (Selvam and Santiago 2007). The second treatment submerged the fiber in 400 mL of NaOH 0.1 M solution (CPNaOH) with agitation for 1 h (Wang *et al*. 2012), and in the last treatment, 2 g of the fiber was placed in 400 mL of $NaClO_2$ solution 1% ($CPNaClO_2$) with agitation for 1 h at 80 °C, after which the fibers were washed with distilled water and were then subjected to kiln drying (Huang and Lim 2006). At the end of the treatments, all fibers were oven-dried for 24 h at 105 °C (± 2 °C). The treated fibers were stored in high-density polyethylene (HDPE) containers and labeled.

Characterization

The FTIR spectra of fibers were performed in a Frontier instrument (Perkin Elmer, Waltham, MA, USA) from 400 to 4000 cm^{-1}, with a resolution of 4 cm^{-1}. The morphologies of the fiber surfaces were characterized in a scanning electron microscope with field emission (SEM-FEG), Zeiss Auriga 40 (Zeiss, Oberkochen, Germany), with a power of 15 kV. The fibers were coated with gold film. The surface wettability to water and oil of fibers was evaluated using a Tensiometer, model K100C (Krüss, Hamburg, Germany).

For oils (crude oil, diesel, marine diesel, new and used engine lubricant, as well as benzene) density was determined using the digital densimeter, model DMA 5000M (Anton Paar, Graz, Austria, Europe) while the viscosity was determined using a rheometer, model

MCR 302 (Anton Paar, Graz, Austria, Europe).

Measurements of oil absorption capacity

The fiber absorption potential was determined based on the method reported by Hilário *et al.* (2019). The absorption capacity was tested for three systems: crude oil alone (Dry), crude oil as a layer on water, simulating an oil spill on the surface of the water (Layer), and water alone. The absorption capacity was tested for three systems: crude oil (Dry), crude oil and water (Layer), and water. Fibers were immersed into the three systems at room temperature (25 °C ± 2 °C) during different time intervals, from 5 to 1440 min. The swollen fibers were removed and drained on a stainless steel screen and weighed. The absorption capacity (g/g), *S*, was calculated according to Eq. 1 (Hilário *et al*. 2019),

$$S = (W_f - W_i) / W_i \quad (1)$$

where W_i (g) and W_f (g) are the mass before and after absorption, respectively.

Reusability

The reuse of the fibers was evaluated by simple compression; 10 mg of the sample was immersed in 5 mL of crude oil for 60 min at room temperature. The fibers were compressed with tweezers, and the resorption capacity was calculated as the ratio of the resorption mass to the initial absorption mass (Hilário *et al*. 2019).

Determination of oil-water selectivity/wettability mobility

The fibers were fixed at the bottom of two beakers with double-sided adhesive tape to evaluate the fibers' oil-water selectivity (Zheng *et al*. 2017). Approximately 100 mL of common diesel and 100 mL of distilled water with dye (methyl blue) were added. Pictures were taken using a digital camera.

RESULTS AND DISCUSSION

Characterization

FTIR spectra

To evaluate the treatments of CP fiber with NaOH, $NaClO_2$ and hydrothermal treatment, the fibers were analyzed by FTIR spectroscopy (Fig. 1). The CP absorption peaks at 3339 cm^{-1}, 2920 cm^{-1}, 1734 cm^{-1}, 1368 cm^{-1}, 1244 cm^{-1}, and 1032 cm^{-1} were characteristic of *Calotropis procera* (Hilário *et al.* 2019). When comparing the spectra of *Calotropis procera* fiber nontreated, $CPNaClO_2$, and CPNaOH, the following results were obtained: a decrease in the intensity of functional groups, including C-H (2920 cm^{-1}), C=O (1734, 1368, and 1244 cm^{-1}), and C-O (1032 cm^{-1}) (Zheng *et al*. 2017). According to Tu *et al.* (2018), this is also concerned with the removal of wax, pectin, and other substances on the surface of the fiber (Lv *et al*. 2017). As observed by Draman *et al.* (2014), attenuations or disappearance of the near peaks corresponding to lignin (1505 and 1597 cm^{-1}) and hemicellulose (1737 and 1248 cm^{-1}) were observed. Such attenuations or disappearances may be related to partial removal of the wax layer from its surface (Mwaikambo and Ansell 2002; Fan *et al*. 2012; Wang *et al*. 2013b). Based on the FTIR spectrum results for CPNaOH and $CPNaClO_2$, the removal of wax, lignin, and hemicelluloses was successful (Draman *et al.* 2014).

For the hydrothermally treated sample (CPHT), there was no obvious variation in other bands except the changes mentioned above.

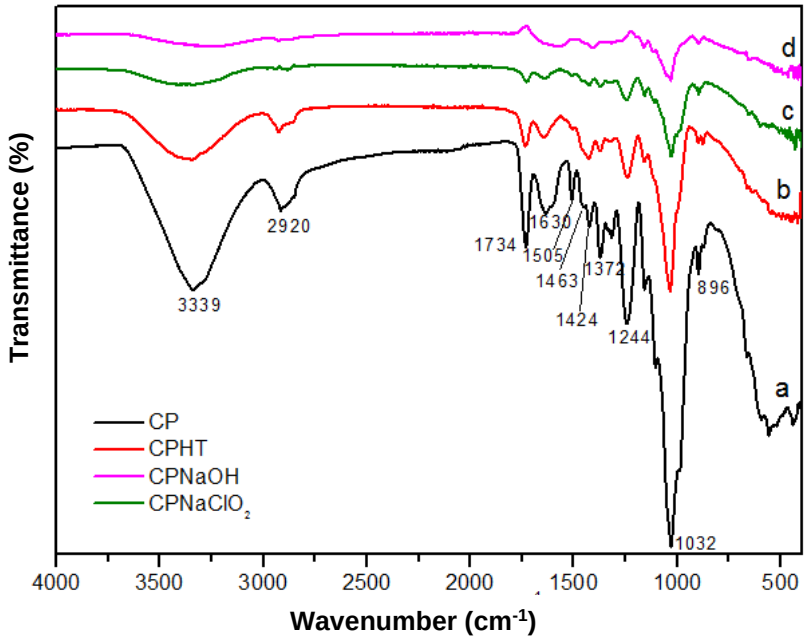


Fig. 1. FTIR spectra of (a) CP, (b) CPHT, (c) $CPNaClO_2$, and (d) CPNaOH

Morphological Analysis – SEM

Figure 2 shows micrographs of CP fibers *in natura* and treated (CPHT, CPNaOH, and $CPNaClO_2$). There were hollow structures in the longitudinal and cross-fiber images, which enables the fixation of the oil and the trap of inter- and intra-fiber structures (van Gelderen 2017) This microstructure aids the buoyancy, as the interior spaces are filled with air.

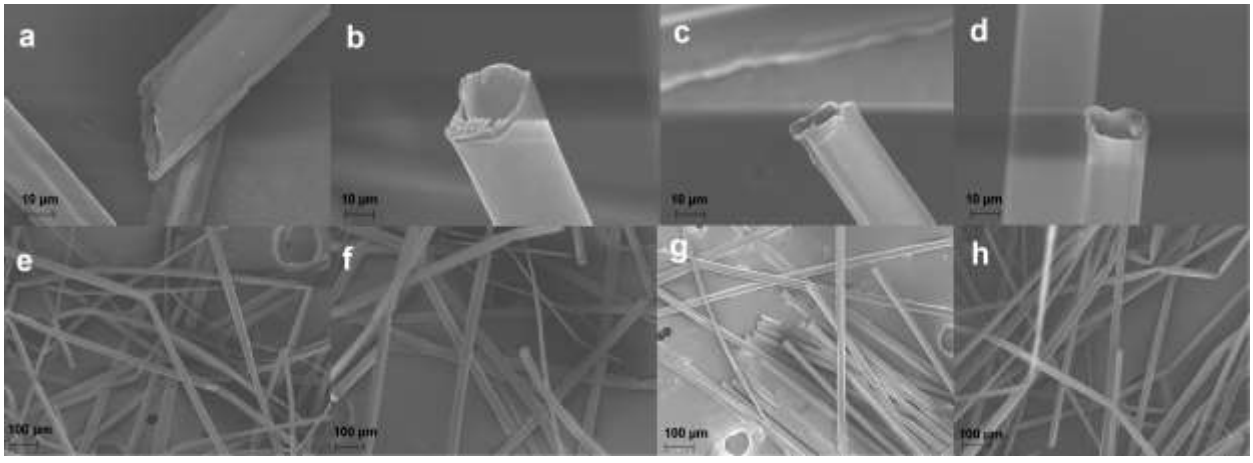


Fig. 2. Micrographs obtained by the SEM-FEG 1000 x (a) CPHT, (b), CPNaOH, (c) $CPNaClO_2$, and (d) CP; 100 x (d) CPHT, (e) CPNaOH, (f) $CPNaClO_2$, and (h) CP

The micrographs (Fig. 2a-d) show a slick surface with hydrophobic waxy coating inside the hollow structure (Nascimento *et al*. 2016; Hilário *et al*. 2019; Song *et al*. 2019). However, no difference was observed on the surface of the treated fibers (Song *et al*. 2019), except in $CPNaClO_2$ fiber, where a flattening was observed after the removal of wax and other extractives. Zhang *et al.* (2014) report the appearance of small debris on the surface

of the *Populus* fiber, attributed to the dissolution of hemicellulose traces and lignin caused by hydrothermal treatment. Wang *et al.* (2012) found that natural fibers, when treated with NaOH, present broken holes and shallow grooves on the surface of their fibrils. Yi *et al.* (2018) compared the tubular structure of *Calotropis gigantea* fiber with $NaClO_2$ to remove part of the wax, resulting in a smoother surface, and also a hollow structure with thin walls. In general, the fibers treated with solution enable the surface to increase and improve oil adhesion to facilitate its entry into the lumen, thus ensuring a high oil absorption capacity.

The diameter, wall thickness, cross-sectional area, and percentage of void fiber space were determined using the Image-J software, from the micrographs of SEM-FEG (Fig. 2e-h) (Thilagavathi *et al*. 2018; Hilário *et al*. 2019). For the calculation of the diameter, 10 measurements of fiber diameters were performed, and the mean and standard deviation was calculated. The results are reported in Table 1.

Table 1. Morphological Details of the Various Fibers

Fiber	Diameter (μm)	Cell Wall Thickness (μm)	Void (%)	Specific Surface Area (m²/kg)
CPNaOH	37.47 ± 3.80	0.633	93	390.8
CPHT	24.56 ± 4.13	0.455	93	161.6
$CPNaClO_2$	27.14 ± 3.55	0.598	91	100.6
CP	23.84 ± 4.44	0.520	91	146.6

The nontreated fiber (CP) had an average diameter of 23.84 ± 4.44 μm, a result similar to the work of Thilagavathi *et al.* (2018) which was 24.70 μm. The fibers treated with CPHT, CPNaOH, and $CPNaClO_2$ had diameters greater than CP, being 24.56 ± 4.13 μm, 37.47 ± 3.80 μm, and 27.14 ± 3.55 μm, respectively. In addition, the CPNaOH presented the largest diameter. Similarly, this fiber presented a larger specific surface area of 390.8 m²/kg, followed by CPHT, CP, and $CPNaClO_2$. The small surface area of the $CPNaClO_2$ fiber can be attributed to the shape of the hollow fiber with the presence of flattened/collapsed lumen (Fig. 2f). The highest percentage of voids was associated with CPNaOH and CPHT fibers, which was 93% hollow lumen, followed by CP and $CPNaClO_2$ fibers.

Oil-absorption capacities

The results of the oil absorption tests are presented in Fig. 3, varying the contact time (5, 20, 40, 60, and 1440 min.). As expected, the absorption increased with time Anunciado *et al.* (2005). Because the CP fiber has large lumens coated with wax, it has high dry sorption capacity for oil between 48.6 and 74.0 g/g, according to Hilário *et al.* (2019). Anunciado *et al.* (2005) obtained similar results in the sorption tests with the increase in the contact time of the oil with the sorbent. The contact time of 24 h (1440 min) presented the highest absorption capacity for crude oil (Fig. 3a).

Removing part of the hydrophobic wax from the surface through hydrothermal treatment and chemical treatment using NaOH and $NaClO_2$ was proposed to improve the absorption capacity of crude oil. The dry absorption capacity for the CPHT, CPNaOH, and $CPNaClO_2$ treated fibers increased by 27.0%, 32.2%, and 21.7%, respectively, when compared to the untreated CP fiber. The CPNaOH presented the highest sorption capacity, 97.9 g/g, followed by CPHT, and $CPNaClO_2$ with 94.0 g/g and 90.1 g/g, respectively, highlighting the absorption capacity and oleophobicity of the fibers. In addition, the treatments increased the diameters (Table 1), consequently, increasing the potential of oil

absorption. The fiber treated with NaOH presented a higher absorption capacity of crude oil (97.87 g/g), which may be related to the 57% increase in the diameter and percentage of empty spaces when compared to CP. Huang and Lim (2006) found that Sumaúma fiber treatment with $NaClO_2$ removed part of lignin, increasing the absorption capacity of various solvents. Zhang *et al.* (2014) observed an increase in oil absorption capacity by dissolving hemicellulose and deposition of lignin droplets by hot water. In addition, hydrothermal treatment greatly increased the surface area of cellulose, observed for CPHT.

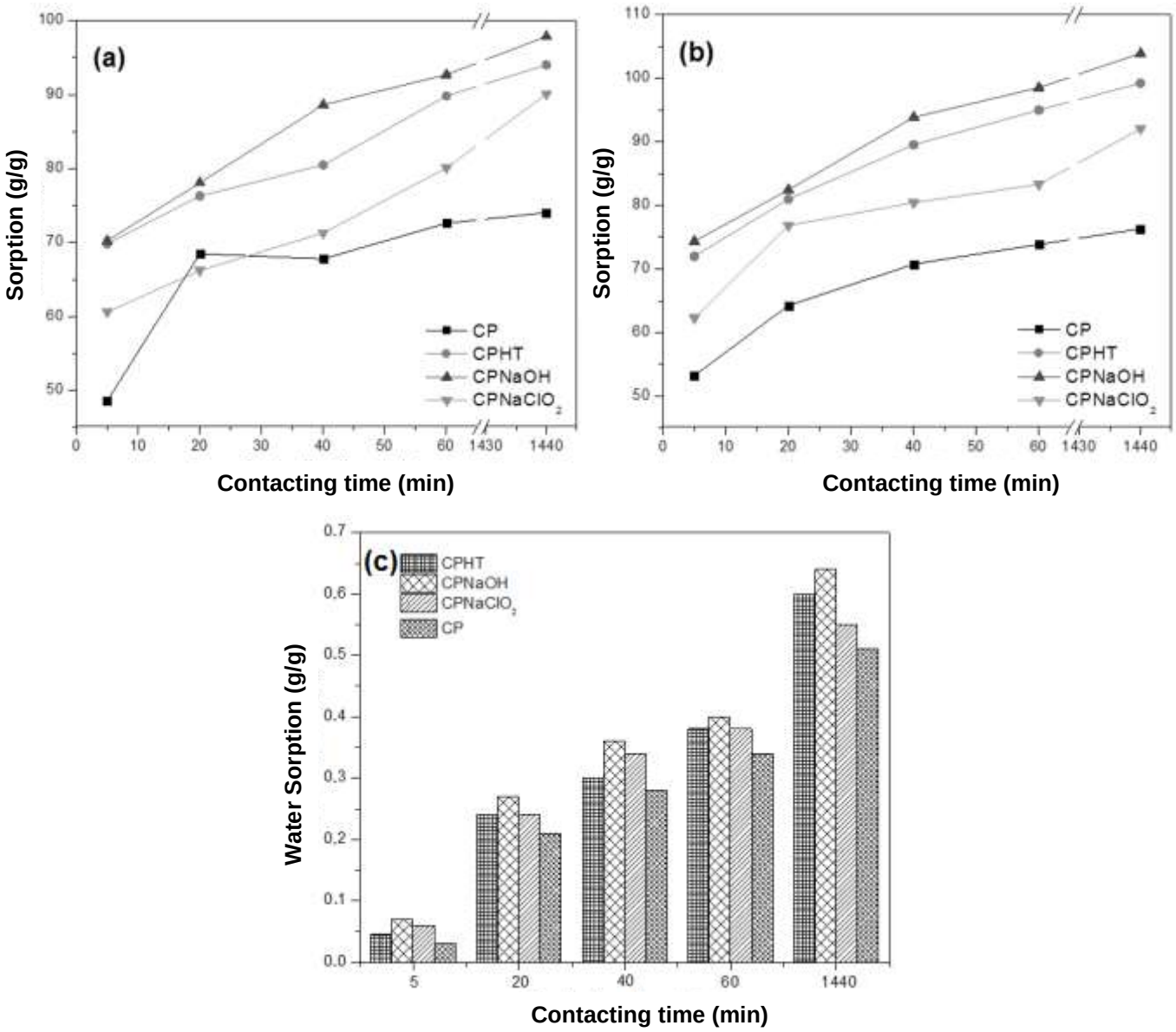


Fig. 3. Absorption test with crude oil (a) dry, (b) oil layer on water, and (c) water sorption

A commonly reported disadvantage of using plant fibers as sorbents in an aqueous medium is the high water sorption (Annunciado *et al*. 2005). However, in the present study, the amount of water sorbed in relation to the crude oil was negligible, showing the hydrophobic and oleophilic character of CP, CPHT, CPNaOH, and $CPNaClO_2$ fibers. As observed in Fig. 3c, CPHT, CPNaOH, and $CPNaClO_2$ fibers absorbed more water when

compared to CP *in natura*, possibly by removing part of the waxy material from the CP surface. The water sorption for the CP, CPHT, CPNaOH, and $CPNaClO_2$ ranged from 0.03 to 0.64 g/g, suggesting a high hydrophobicity of the treated fibers. In addition, as expected, water sorption also increased over time, and all water sorption values were subtracted from the results of the layer tests.

Table 2. Absorption Percentage for the Several Contact Times in Relation to the Time 1140 min for the Dry and Layer Systems

System	Contact Time (min)	CP	CPHT	CPNaOH	$CPNaClO_2$
Dry	5	66%	74%	72%	67%
	20	92%	81%	80%	74%
	40	92%	86%	91%	79%
	60	98%	96%	95%	89%
	1440	100%	100%	100%	100%
Layer	5	70%	73%	72%	68%
	20	84%	82%	79%	83%
	40	93%	90%	90%	87%
	60	97%	96%	95%	91%
	1440	100%	100%	100%	100%

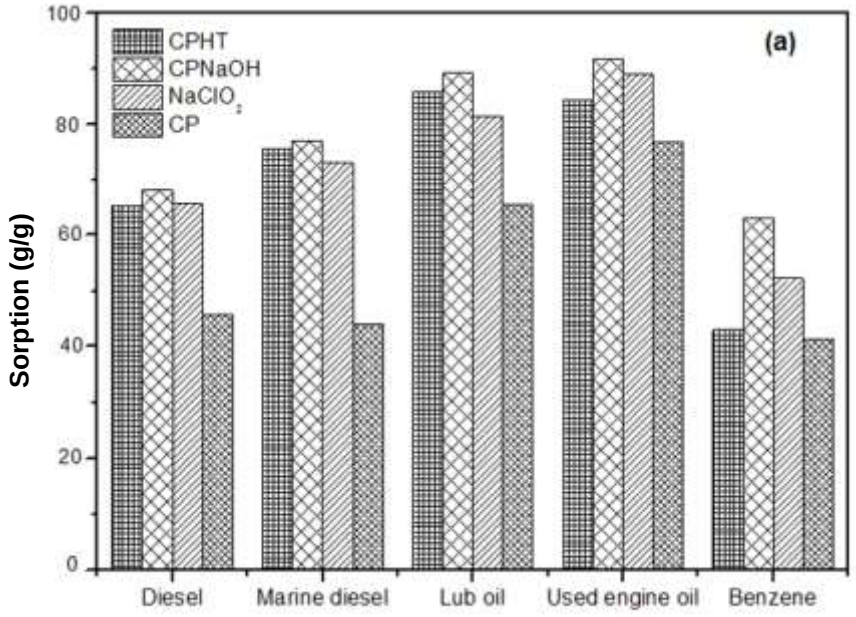
Table 2 shows the percentage of absorption reached by several contact times in relation to the maximum absorption after 1440 min (24 h) for dry and layer systems. For the dry system, 65% of the absorption capacity for the time of 1440 min was accumulated during the first five minutes, remaining in an interval between 66% and 74%. According to Annunciado *et al.* (2005), most absorption occurs in the first minutes for the studied fibers, followed by a slow increase in the absorption values over time, *i.e.*, much of the absorption potential of the fibers is achieved in a short interval of time. Most of the fibers used in this work reached at least 90% of their maximum absorption capacity in 60 min, except for the $CPNaClO_2$, which was 88.9%. In total, regardless of absorption conditions (dry or layer), the test at an absorption time of 24 h showed an absorption capacity of 76.3 g/g for the CP wire (Hilário *et al*. 2019), 99.2 g/g for CPHT, 103.9 g/g for CPNaOH, and 92.0 g/g for $CPNaClO_2$. This sorption capacity is much higher than those reported for other plant fibers in the literature. In the layer system (Table 2), the absorption percentages exceeded 67% of the maximum absorption capacity in the first five minutes for all fibers. In addition, all fibers reached at least 90% of their 24-hour sorption capacity in just 60 min. In cases of oil spills, the less time the authorities spend cleaning/removing contaminants, the lower the impact generated on the environment. As observed, the contact time of 60 min presented approximately 90% of the maximum sorption capacity obtained after 1440 min. Only $CPNaClO_2$ presented 89% of the maximum capacity after 60 min. Thus, the fibers are more efficient in the contact time of 60 min, in cases of real environmental accidents. Thus, considering the influence of the oil characteristics in the absorption capacity, diesel, marine diesel, new and used engine lubricant as well as benzene were evaluated in the absorption capacity test using the fibers CP, CPHT, CPNaOH, and $CPNaClO_2$ for a contact time of 1440 min and dry system. Table 3 listed the proprieties of oil and organic solvent.

Table 3. Properties of the Oils and the Organic Solvents

Sample	Density at 20 °C (kg/m³)	Viscosity (cP)
Diesel	813	1.953
Marine Diesel	825	2.375
New engine lubricant	850	62.73
Used engine lubricant	854	69.25
Benzene	808	0.484
Crude oil	861	73.60

The results are presented in Fig. 4a. In the dry test of CPHT fibers, CPNaOH and $CPNaClO_2$ had absorption capacities greater than CP for all oils and solvent that were tested. Karan *et al.* (2011) presented in their studies the viscosity of the oil as a parameter of great importance in the sorption process. In general, an increase in the viscosity of the oil reduces the sorption within the pores and capillary vessels, but on the other hand, more viscous oils have higher sorption due to adhesion to the surfaces of the materials. Therefore, Fig. 4b confirms a lower absorption capacity for diesel, marine diesel, and benzene when compared to lubricating oils and crude oil.

Hilário *et al*. (2019) demonstrated (CP) that oils are adsorbed by hydrophobic interactions and capillary action forces that penetrate the lumen through the inner capillary. The amount of oil retained within the CP also depends on the oleophilicity of the fiber and physical characteristics of the oil (Hilário *et al*. 2019).



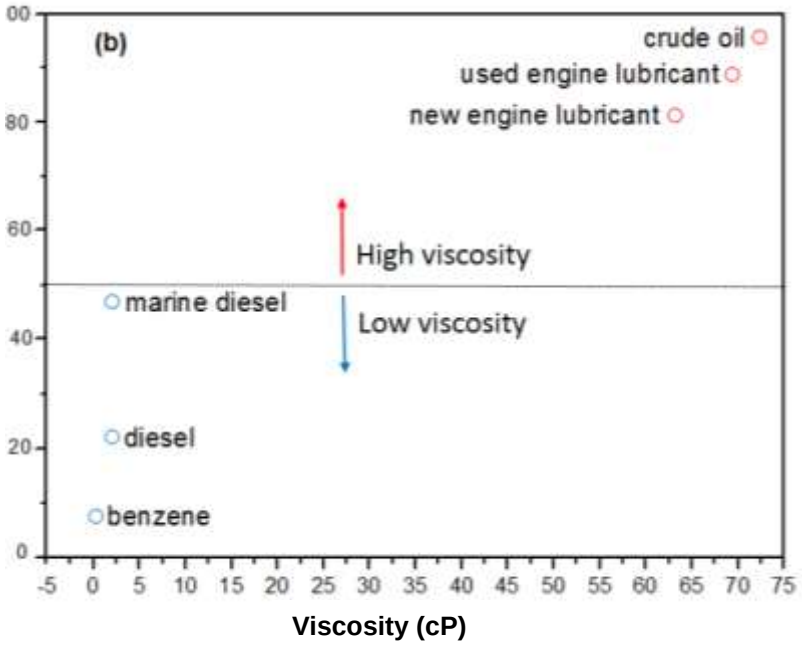


Fig. 4. Dry oil absorption test (a) comparing CP with CPHT, CPNaOH, and CPNaClO$_2$ for a contact time of 1440 min, and (b) effect of viscosity in absorption for different oils and organic solvent for a contact time of 1440 min

In addition to the high oil absorption capacity and fast absorption, good reuse capacity is also necessary for the development of an excellent oil sorbent. Thus, to evaluate the reuse capacity of CP, CPHT, CPNaOH, and CPNaClO$_2$ fibers, simple compression was used during 6 cycles; the results are shown in Fig. 5. After the first recycle test, the CP, CPHT, CPNaOH, and CPNaClO$_2$ resorption was about 82%, 85%, 83%, and 89% of crude oil, demonstrating that fibers can be well reused for another oil absorption test.

The average resorption capacity of fibers after 6 cycles was above 50% of oil when compared to the initial absorption. A mass total of 445.8 g of crude oil per gram of CPNaOH fiber was removed after 6 resorption cycles, demonstrating that the treated fiber has a reuse potential.

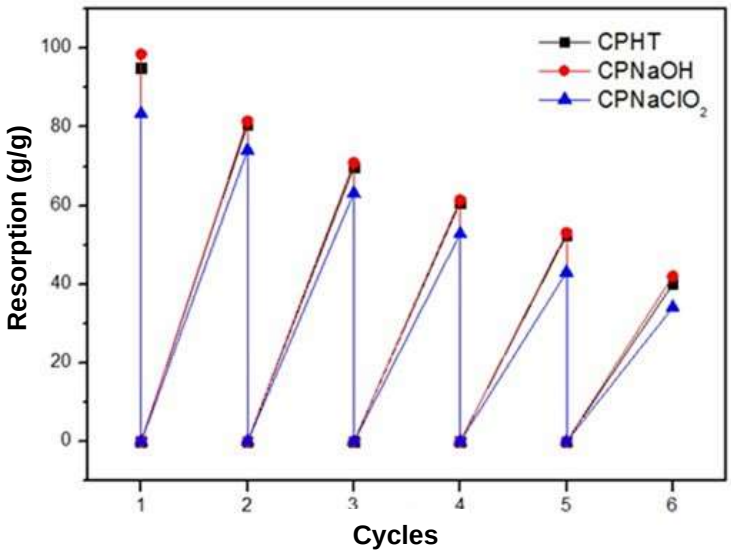


Fig. 5. Resorption test for the crude oil using fibers CP, CPHT, CPNaOH, and $CPNaClO_2$

Wettability

Figure 6 displays the record of the selectivity test using CPNaOH fiber. The fiber wettability was verified by the contact angle between the surface of the fiber with water or diesel drop, to confirm the hydrophilic and hydrophobic properties. As shown in Fig.s 6a-b, the contact angle was visible on the surface of CPNaOH, and the contact angles (θ) were 0^o and 114°, for diesel and water, respectively. These results demonstrated hydrophobicity and oleophobicity.

The wettability test was also recorded with the aid of a digital camera. The CPNaOH was placed on a glass plate, and about 2 μL of diesel or distilled water with methyl blue dye was dropped using a microsyringe (Fig. 6a-b). When diesel came into contact with CPNaOH, it was fully absorbed (Fig. 6b), while the distilled water was free on the fiber surface formed spherical drops (Fig. 6a).

The CPHT and $CPNaClO_2$ contact angles were 121° and 119°. There was a greater decrease in the water contact angle for CPNaOH. This was a consequence of alkali treatment and, possibly, a greater reduction in the waxy surface of the fibers, also evidenced by the infrared spectra (Fig. 2) due to the decrease in the intensity at 2920 cm^{-1} that is associated to the CH stretch, and in the water sorption test (Fig. 3c).

The fiber was taped to the bottom of a 100 mL glass beaker with double-sided tape to evaluate the selectivity of CPNaOH. When water was added (Fig. 6c-d), a silver reflex appeared on the surfaces of the fibers. This phenomenon is attributed to the presence of a thin air layer, which can form a reflection on the surfaces of the fiber (Fig. 6b) (Zheng *et al*. 2017). The same procedure was performed with diesel oil, where the swelling of CPNaOH was observed when the diesel oil was absorbed, showing selectivity to oil (Fig. 6e).

Table 4. Absorption Percentage for the Several Contact Times in Relation to the Time 1140 min for the Dry and Layer Systems

Sorbent Material	Treatment	Sorption capacity (g/g)	Oil	Reference
Kapok fiber	*In natura* Water NaOH HCl $NaClO_2$ Chloroform	30 34 32 35 24	Toluene	Wang *et al.* 2012
Kapok Fiber	Packed	36 43 45	Diesel Hydraulic oil Motor oil	Lim and Hung 2007a
Calotropis gigantea fiber	Nickel	45 to 120	Oil and organic solvents	Cao *et al.* 2018
	Copper	45 to 105		
	In natura $NaClO_2$ + Carbonized	60.59 84.71	Kerosene	Tu *et al.* 2018
	In natura	22.6 to 47.6	Oil and organic solvents	Zheng *et al.* 2016
Barley straw	Pyrolyzed	5.9 to 7.6 8.1 to 9.2	Diesel Heavy oil	Husseien *et al.* 2008
	Surfactant-modified	30 to 90 15 to 95	Canola oil Mineral oil	Ibrahim *et al.* 2009
Silkworm cocoon	Cocoon residues	42 to 52 37 to 60	Motor oil Vegetable	Moriwaki et al. 2009]
Cotton fiber	Loose fiber Fiber pad shape	22.5 18.43	Lubricating oil	Husseien *et al.* 2011
Peat	Graft add-on	36.60 25.56	Crude oil Vegetable oil	AlAmeri *et al.* 2019
	Granular	9 to 12	Diesel	Cojocaru *et al.* 2011
Populus fiber	Hydrothermal Acetylation	16.78 21.57	Corn oil	Zhang *et al.* 2014
Celulose aerogel	Methyltrimetoxissyan	40 to 95	Oil	Feng *et al.* 2015
Ganoderma applanatum mushroom	PFOCTS*	1.8 to 3.1	Oil	Balzamo *et al.* 2019
Hybrid of cotton, Kapok, *Asclepias Syriaca*, *Calotropis procera*, *Calotropis gigantea* Polypropylene	Hybrid	40.16 23.00	Heavy oil Diesel	Thilagavathi *et al.* 2018
Calotropis procera	*In natura* Thermal	74.04 94.31 to 124.60	Crude oil	Hilário *et al.* 2019
	Hydrothermal NaOH $NaClO_2$	99.20 103.90 92.04	Crude oil	This Research

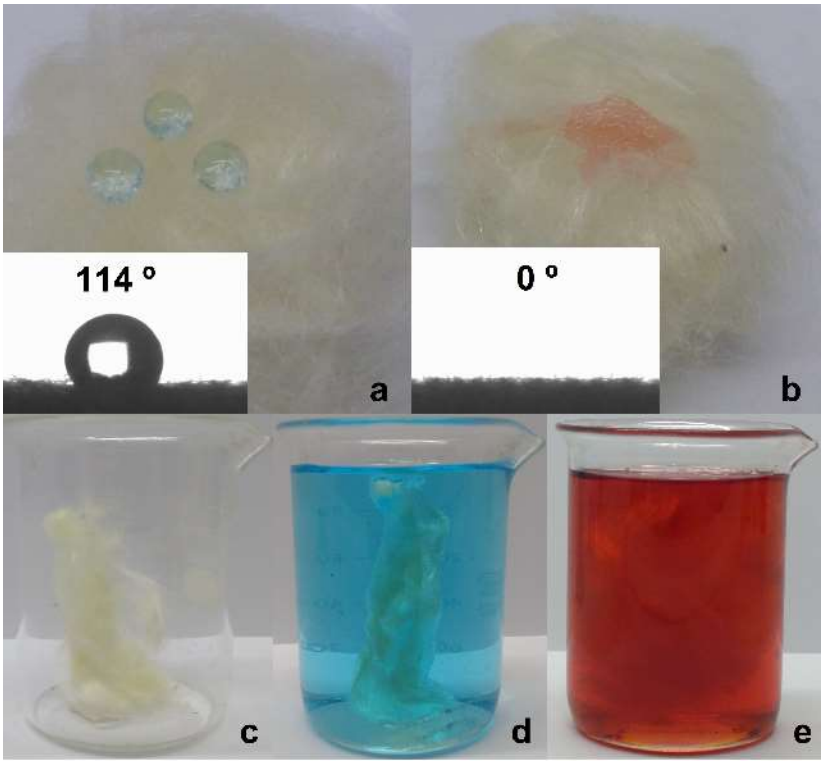


Fig. 6. Digital images of the wettability and selectivity test: (a) water (b) diesel oil; Selectivity essay: (c) CPNaOH, (d) CPNaOH immersed in water, and (e) CPNaOH immersed in diesel oil

Advantages of treated Calotropis process over other materials

In general, the absorption capacity of crude oil by the *Calotropis procera* fiber treated with solutions was equal and even higher than those presented by most sorbents reported in dry tests. Table 4 presents the sorption capacity of organic oils and solvents for various sorbent materials that have suffered modification processes to obtain better results. The CP treated with NaOH, $NaClO_2$, and hydrothermally presented a high absorption capacity for the crude oil used in this work. One can observe that some materials have higher absorption capacity, such as the thermally treated CP fiber (Hilário *et al.* 2019). The treatment with NaOH significantly increased the internal diameter and surface area of the CP lumens, allowing the increase of absorption capacity, being a promising alternative against synthetic oil absorbers traditionally applied in the oil spill cleaning process.

CONCLUSIONS

1. *Calotropis procera* (CP) fibers that had been either hydrothermally treated (CPHT), treated with 0.1% NaOH (CPNaOH), or treated with 1% $NaClO_2$ ($CPNaClO_2$) presented high hydrophobicity, oleophobicity, and selectivity for oil, which was confirmed by contact angles of predominantly hydrophobic surfaces, θ of 121°, 119°, 114° in water, and 0^o for diesel oil.
2. FTIR spectra pointed out that after treatments of fibers in solution (CPHT, CPNaOH, and $CPNaClO_2$), there was a decrease and disappearance of some peaks, which may be correlated with partial removal of the wax.

3. Micrographs obtained by SEM-FEG equipment revealed the surface morphology of the CP, CPHT, CPNaOH, and CPNaClO$_2$ and showed the presence of hollow structures, wherein the lumens contribute significantly to oil fixation. However, at the end of treatment in solution, sorption was observed the increase within the cell walls and empty spaces (lumens), increasing the oil absorption potential of the fibers.
4. In the dry system absorption test, the fibers treated with the solutions showed an increase in oil absorption from 21.7% to 32.2% when compared with untreated CP.
5. Tests carried out with a of oil on water showed the general absorption profile, CPNaClO$_2$ < CPHT < CPNaOH, with maximum sorption capacities of 92.0, 99.2, and 103.9 g/g.
6. It was also observed that in the contact time of 5 min in the dry and layer system, the absorption values of the fibers had exceeded 65% and 67%, respectively. After 60 min of exposure, the absorption of most fibers in both systems exceeded 90% of their absorption capacity for the contact time of 1440 min.
7. Based on this work, the CP, CPHT, CPNaOH, and CPNaClO$_2$ fibers can be used as a successful alternative for cleaning and removing crude oil and petroleum derivatives from leaks and spills, once that it has an excellent selectivity water/oil, high availability, reuse capacity, and high oil absorption.

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