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ORIGINAL PAPER

Producing aerogels from silanized cellulose nanofiber suspension

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Abstract Aerogels from biodegradable and renewable sources such as cellulose, for example, have become a promising alternative to separate oil from water. However, surface treatments are necessary to provide hydrophobic characteristics to the sorbents. This study aims to evaluate the chemical treatment of cellulose nanofibers (CNFs) with methyltrimethoxysilane (MTMS), in order to obtain hydrophobic sorbents to be used in the removal of oil spills from aquatic environments. CNFs were obtained from cellulose pulp waste by mechanical grinding, with a fiber diameter ranging from 40 to 66 nm. Four different chemical treatment methodologies were tested. The treatment of CNFs with MTMS using mechanical stirring at 500 rpm for 1 h, at 70 °C for 2 h, followed by freeze drying was the most effective one to obtain hydrophobic CNF aerogels. The samples presented a contact angle with water of 133.51°, sorption capacity in heterogeneous medium of 16.78 g g^{-1}, and oil removal efficiency of 87.9%.

Keywords Cellulose nanofiber (CNF) · Aerogel · Organosilane · Freeze drying · Oil sorption

Introduction

According to the Yearbook of the National Petroleum Agency, Brazil has 154 oil exploration wells in marine waters, which corresponds to approximately 96% of a total of 31 billion barrels of Brazilian oil reserves. The increase in the exploration of this commodity requires transportation, which also increases the risk of oil spills. In this context, it is important to develop ways to

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contain and mitigate the effects of water pollution caused by oil spills (ANP 2015).

Aiming to overcome this issue, several methods have been proposed to treat oil contamination in water, as follows: sorption processes, coagulation, flocculation, electrocoagulation, chemical degradation, gravimetric separation, filtration processes, coalescence (depth filtration) and combustion (Wahi et al. 2013; Liu et al. 2014). Sorption processes are widely used for oil spill removal from water. This technique presents advantages over the aforementioned methods, such as its simple application, high, quickly and effective sorption capacity, good selectivity, low density and possibility to be obtained from renewable sources (Ibrahim et al. 2009; Liu et al. 2014). Recently, sorbent materials derived from cellulose fibers have become a viable alternative to synthetic sorbent materials.

Cellulose is the most abundant biopolymer in the world, with global reserves of up to 7.5×10^{10} tons, totaling about 40% of the plant biomass (Chen et al. 2011; Jia et al. 2014). The production of cellulose in Brazil presents an average annual growth of 7.5%, having reached the fourth position in the world rankings in 2008, with 16.5 million tons produced in 2014. Brazil is currently the largest producer of short fiber cellulose (IBÁ 2015).

Cellulose $(C_6H_{10}O_5)_n$ is a long-chain polymeric polysaccharide of glucopyranoses with repeating units linked by β-1,4 glycosidic bonds (Taipale et al. 2010; Abdul Khalil et al. 2012; Song et al. 2014). The van der Waals and intermolecular hydrogen bonds in cellulose promote the parallel stacking of the chains, and so they aggregate to form small fibrils with diameter ranging from 5 to 50 nm and several micrometers in length. In this context, one can obtain cellulose nanofibers (CNF) through top-down processes from cellulose fibers that have already undergone bleaching and delignifying steps solely by mechanical processes such as high pressure homogenization, microfluidization or grinding (Zimmermann et al. 2016). CNFs have diameters of less than 100 nm and lengths of several microns. According to Nakagaito et al. (2013) the greater number of exposed hydroxyl groups available for bonding due to the nanoscale morphology in CNFs produces much enhanced bonding forces. Because of their reduced size and theoretical high surface area, CNFs make a promising starting material for sorbents.

Sorbent materials from cellulose fibers can sorb liquids in large quantities; however, they present a hydrophilic character. To modify this characteristic and turn these materials into hydrophobic ones, it is necessary to perform a suitable treatment to obtain a material with ability of adsorbing oil in aquatic environments. The hydrophilic character of cellulose can be altered by using coupling agents that react with the hydroxyl groups present on the fiber surface. The most cited processes to achieve this modification include the use of organosilanes (Cervin et al. 2012; Zhang et al. 2014; Jin et al. 2015). Tarrés et al. (2016) prepared aerogels from three types of CNF obtained by TEMPO oxidation, enzymatic hydrolysis and mechanical pulping. The hydrophobization of CNF was done by addition of alkyl ketene dimer (AKD) and the CNFs were subsequently freeze dried. Zhang et al. (2014) obtained nanocellulose through homogenization processes and produced sponges prepared by freeze-drying CNF-based aqueous suspensions containing MTMS as a silylating agent. In this case, only one silylation process without the use of heat was performed. At a 1.5% (wt%) CNF content, the aerogels displayed adsorption values of approximately 50 g g^{-1} with motor oil (Shell Rimula Oil 30) and up to 102 g g^{-1} with chloroform in heterogeneous media.

Some of the published studies in this area also focus on obtaining cellulose aerogels by using solvents for gelation. Gavillon and Budtova (2008) obtained aerogels from cellulose in aqueous medium with sodium hydroxide, and dried the aerogels by supercritical drying with CO_2. Nguyen et al. (2014) obtained aerogels from recycled cellulose fibers dispersed in NaOH/urea by sonication, freeze-drying and then vapor deposition of organosilanes.

To the best of the authors' knowledge, there is little literature related to the development of aerogels produced from CNFs without a previous gelation process. As such, the novelty of this work is the development of hydrophobic CNF aerogels obtained from bleached cellulose pulp residues by mechanical grinding only, and to chemically treat them with organosilanes. According to Xie et al. (2010), in most cases, organosilanes undergo a chemical reaction with cellulose fibers at high temperatures. As such, it is important to test several parameters in silylation processes. Four silylation methodologies were tested, with varying temperature and agitation, to evaluate the influence of these conditions in the silylation of the aerogels with MTMS. The chemical composition, morphology, contact angle measurements and sorption capacity in aqueous, oil and heterogeneous media were evaluated.

Materials and methods

Materials

Dried cellulose plates of *Eucalyptus* sp. species were provided by Celulose Riograndense (RS, Brazil). Acetic acid P.A was provided by Neon and methyltrimethoxysilane (MTMS) 98% purity was purchased from Sigma-Aldrich. All reagents were used as received without purification.

For the sorption experiments, the SAE 20W50 motor oil provided by Ipiranga Petrochemical was used, with a viscosity of 64 cSt, density (20–40 °C) of 0.88 g cm^{-3}, classified as medium oil according to ASTM F726-12.

Methods

Obtainment of the CNFs suspension

The CNFs suspension was obtained by mechanical fibrillation. The cellulose plate was ground in a grinder (Masuko Sangyo-MKCA6-2J) for 5 h with recirculation to obtain a homogeneous suspension with a concentration of 3% (w/v) in water (Zanini et al. 2016). Figure 1 illustrates the fibrillation process. Cellulose fibers are forced to pass between the silicon carbide discs, and one of the discs rotates and the other remains static with grooves on the surface.

Chemical treatment with organosilane

The CNFs suspension was filtered through a vacuum system. The pH of permeate was then adjusted to 3 by adding acetic acid under magnetic stirring for 5 min. Subsequently, 2% in mass of MTMS was added to this solution under magnetic stirring. The pH adjusting process is necessary to promote the hydrolyzation of the MTMS, and to form the silanol groups that will later react with the cellulose nanofibers. According to Xie et al. (2010), cellulose is not reactive to many chemicals, and the OH groups are many times not accessible. Generally, the hydrolysis of organosilanes under acidic pH conditions favors the formation of more reactive silanol groups as well as the retardation of their condensation rate, which makes them available to react with the OH groups of the fibers, or to condensate over the fiber surface.

The resulting solutions were added dropwise slowly into the MTMS supernatant filtration. Four methodologies for the chemical treatment of CNFs suspension were tested, adapted from Zhang et al. (2014) and Nguyen et al. (2014), as shown in Fig. 2.

Triplicates of the samples obtained in the chemical treatment were weighted (30 g) and placed in metallic molds of approximately 45 mm in diameter and 25 mm in height, to proceed to freeze drying. The samples were frozen at −80 °C with liquid nitrogen and transferred to a vacuum chamber for the freeze drying process (Lio Top—L 101).

Sample characterization

The modification on the aerogels surface was investigated by FTIR (Nicolet IS10, Thermo Scientific). Each spectrum was obtained by performing 32 scans by attenuated total reflection (ATR). The wavenumber range analyzed was 400 to 4000 cm^{-1}.

Fast sorption tests in homogeneous medium were performed as adapted from ASTM F726-12. The samples were obtained with a diameter of 43.7 ± 0.25 mm and a thickness of 17.9 ± 0.54 mm. The aerogels were maintained in a room with controlled temperature of 23 ± 4 °C prior to the test. The samples were weighed and placed in homogeneous media (either water or oil) for 15 ± 0.5 min. After that, the aerogels were vertically removed from the media and were drained for 30 ± 2 s, and then weighed. Triplicates were performed. The sorption capacity results were calculated according to Eq. (1), and the results were expressed as quantity of absorbed oil by mass of the absorbent material.

$$\mathrm{CA} = \frac{\mathrm{m_f} - \mathrm{m_i}}{\mathrm{m_i}} \tag{1}$$

where CA = sorption capacity (g/g), m_i = initial mass (g), m_f = final mass (g).

The contact angle measurement was obtained through the sessile drop method, in distilled water, with an approximate droplet volume of 5 µL. The samples were placed on a glass slide, at 25 ± 2 °C and relative humidity of 60 ± 5%. Three droplets of water

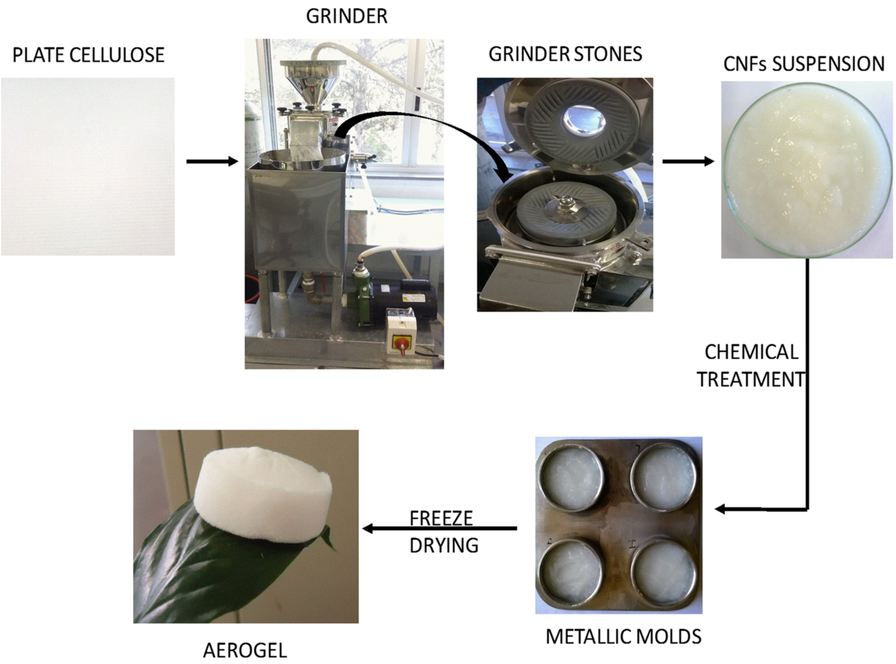

Fig. 1 Representation of the mechanical grinding and freeze drying processes used to obtain the CNF aerogels

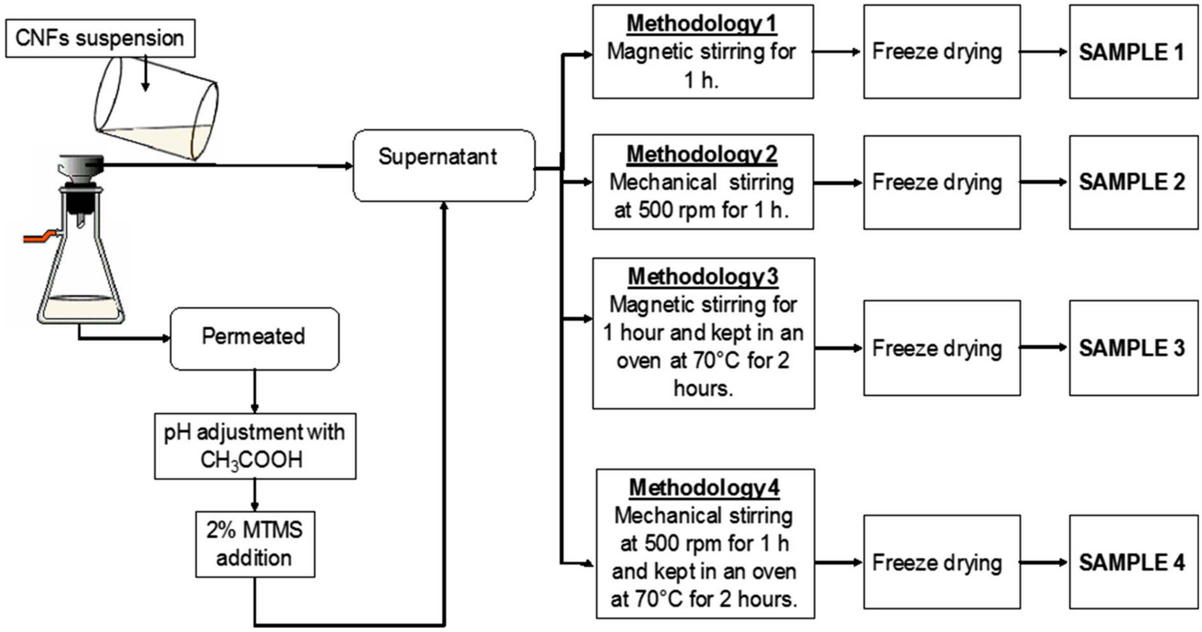

Fig. 2 Fluxogram of the chemical treatment and different agitation and temperatures used in the four methodologies

were placed on the top of the samples. The pictures were recorded every 5 min for 30 min. The images were analyzed with the Surftens software.

The sorption test on heterogeneous medium (oil and water) was performed based on the amount of oil absorbed by the sample in the quickly sorption test on homogeneous (oil) medium. The previously estimated quantity of oil, based on the fast sorption test in homogeneous medium (oil), was added to a Petri dish with 200 mL of distilled water. After that, the aerogels were put in the heterogeneous medium for 15 ± 0.5 min. The sorbent was removed from the oil in a vertical orientation with a clip, leaving it to drain for 30 ± 2 s and weighed according to the ASTM F726-12 standard adaptation. The assays were performed in 3 samples and the amount of oil adsorbed is given by Eq. (1). This method was adapted from adapted from Zhang et al. (2014) and Nguyen et al. (2014).

Scanning electron microscopy with field emission gun (FEG-SEM-MIRA 3, Tescan) was used for morphological characterization of the aerogel and measurement of the fiber diameters.

Results and discussion

Obtaining the CNF suspension

The mechanical fibrillation of cellulose yielded an homogeneous suspension which was white and opaque in color (Fig. 3), a common characteristic of nanofibrillated cellulose suspensions.

The contact of the fibers with the grooves on the surface of the stones, combined with repeated cyclical tensions and centrifugal forces, results in fiber fibrillation (Abe et al. 2007; Kalia et al. 2014). According to Siró and Plackett (2010), the strong shear forces cause the breakage of the hydrogen bonds present in the structure of the cell walls of the cellulose, which also contributes to the obtainment of fibrils in the nanometric scale, yielding an opaque gel.

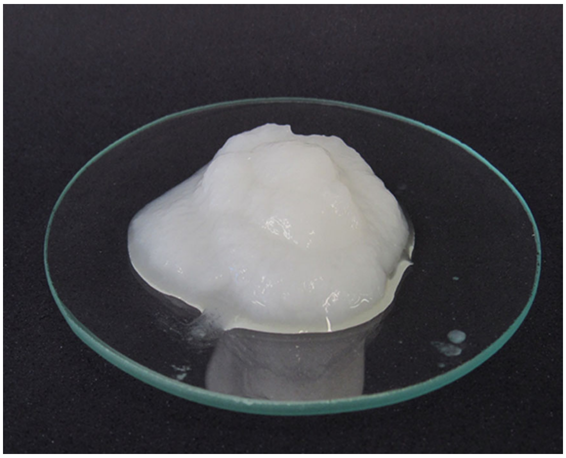

Fig. 3 Visual aspect of the CNF gel obtained by mechanical grinding

Fourier transform infrared spectroscopy (FTIR)

The chemical alterations on the surface of the samples were evaluated, and Fig. 4 shows the FTIR spectra obtained for all samples. The main peaks and bands for cellulose and silanes were highlighted.

All samples display the common peaks for cellulose. The band at 3343 cm^{-1} is related to the stretching vibration of O–H bonds of the hydroxyl groups of cellulose and absorbed water. The peak at 2885 cm^{-1} represents the C–H stretching vibration, and the band at 1421 cm^{-1} represents the symmetrical bending of the CH_2 groups of cellulose. The absorbance peak at 1160 cm^{-1} is due to the anti-symmetrical deformation of the C–O–C bond of cellulose. The peak at 1311 cm^{-1} corresponds to the symmetrical bending of the C–H and C–O groups, and between 1030 and 1025 cm^{-1} is related to the C–O deformation at C_6 in cellulose, (Popescu et al. 2009; De Rosa et al. 2011; Chen et al. 2015; Lavoratti et al. 2016). After the MTMS treatment, some peaks and bands related to silane were identified in Sample 4 as follows: at 1270 cm^{-1}, related to the bending of the C–H bonding of the methyl groups; between 970 and 850 cm^{-1}, corresponding to the stretching vibration of the Si–OH bonding in the silane groups; and between 830 and 730 cm^{-1} (ν(Si–C)), related to the stretching vibration of the Si–C or the Si–O bonds (Ozmen et al. 2007; Zhang et al. 2014).

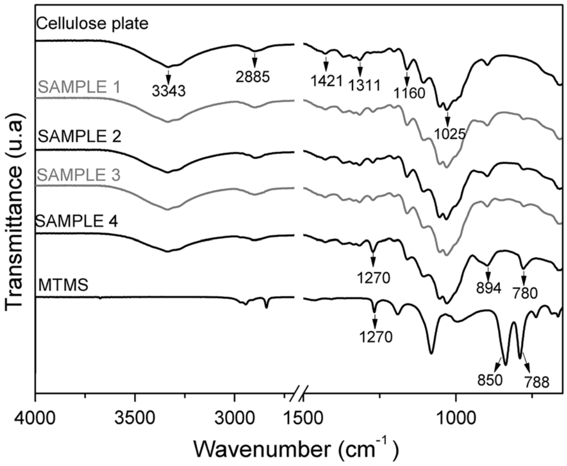

Fig. 4 FTIR spectra of the neat cellulose plate, the four samples obtained through each silylation methodology, and the MTMS silane

No changes in the intensity of the 3343 cm^{-1} band were visible. This happens due to the fact that the organosilanes do not react with all of the hydroxyl groups present in the material. This behavior was also observed by Sai et al. (2015).

Sorption tests in homogeneous medium (water)

Sorption tests were performed in aqueous medium and four samples, one for each silane deposition methodology, were tested. The absorption capacities of the samples were 29.833 ± 0.089 g g^{-1}; 29.995 ± 0.078 g g^{-1}; 28.807 ± 0.064 $g.g^{-1}$ and 0.250 ± 0.013 g g^{-1} for Samples 1, 2 3 and 4, respectively. Samples 1, 2 and 3 showed great affinity with water, namely, they presented a hydrophilic character. This denotes that the methodologies used were not efficient. Sample 4, on the other hand, absorbed only a fraction of water compared to the other samples, which evidences a low affinity with water.

In chemical treatments, both the stirring methods (magnetic or mechanical) and the temperature (70 °C for 2 h) influenced in the silylation process. The mechanical stirring coupled with the increase in temperature favored the coupling of MTMS on the fibers in the suspension, allowing Sample 4 to absorb less water, while Samples 1, 2 and 3 absorbed more than 28 times its own weight in water. According to Xie et al. (2010), heating promotes the condensation of free silanol groups, which results in the formation of polysiloxane layers on the fibers' surface, which reduces the surface energy (Cervin et al. 2012), and the entangled polysiloxane networks in the cell walls. In addition to that, according to Hubbe et al. (2008), the reaction of the silanol groups of MTMS with the hydroxyl groups of cellulose occurs in the presence of humidity and temperature.

Figure 5 illustrates the results obtained with this silanization method. Droplets of oil and water were placed on the top of the Sample 4, and the behavior of Samples 1, 2 and 3 and Sample 4 in water is also shown.

Sample 4 displayed the capacity to repel water and to absorb oil, thus confirming its hydrophobic character that can also be observed in the Supplementary material 1. This characteristic allows the low water absorption in the separation of oil in aqueous medium, preventing the collapse of the microstructure of the material due to water absorption. It also displays more efficiency when absorbing oil in a single cycle, facilitating the separation process (Annunciado et al. 2005; Likon et al. 2013).

The chemical treatment with MTMS provides oleophilic and hydrophobic properties to the nanocellulose aerogels. According to Xie et al. (2010), reactive silanol groups are physically absorbed by hydroxyl groups of cellulose though hydrogen bonds. These groups also react with each other to form Si–O–Si and Si–O–C bonds, promoting the hydrophobization of the aerogel surface (Xie et al. 2010). This is one of the possibilities that may have occurred in this study, as evidenced by the modifications in the CNF surface reported in the FTIR results, where it is observed that the peaks and bands related to the stretching vibration of the MTMS functional groups appeared.

Contact angle measurement

Figure 6 shows the contact angle measurement test for Sample 4, which was the only sample that displayed a degree of hydrophobicity and surface modification, as shown in the FTIR spectra and Fig. 4. The contact angle measurement on the aerogel surface, in this case, is defined as the angle between the solid surface and the tangent of the liquid phase on the interface of the solid phase. The contact angle measurements were not possible to be done for Samples 1, 2 and 3, due to their immediate absorption of the water droplets.

The contact angle obtained for this sample 4 was 133.51° ± 1.89°. This value is close to that found by Nguyen et al. (2014) for hydrophobic aerogels obtained by vapor deposition of MTMS. The authors obtained a value of 135.20°. Zhang et al. (2014) obtained a value of 136° for nanocellulose aerogels. The angle of 136° ± 2° using trimethylchlorosilane (TMCS) was also found by Jin et al. (2015), but the authors used the vapor deposition process. With another type of reagent (AKD—2 wt%), Tarrés et al. (2016) reported an angle of approximately 120°.

In theory, the higher are the values of the contact angle, the higher is the affinity of aerogels to oils, thus indicating more efficiency and more hydrophobicity, facilitating the initial stages of oil sorption. These results are in accordance with the water sorption tests. Since the silanol functional groups are present on the surface of the fiber, hydrophobicity is expected, thus the contact angles are high (Wu et al. 2013). It is also noted that, after 30 min, the contact angle remains

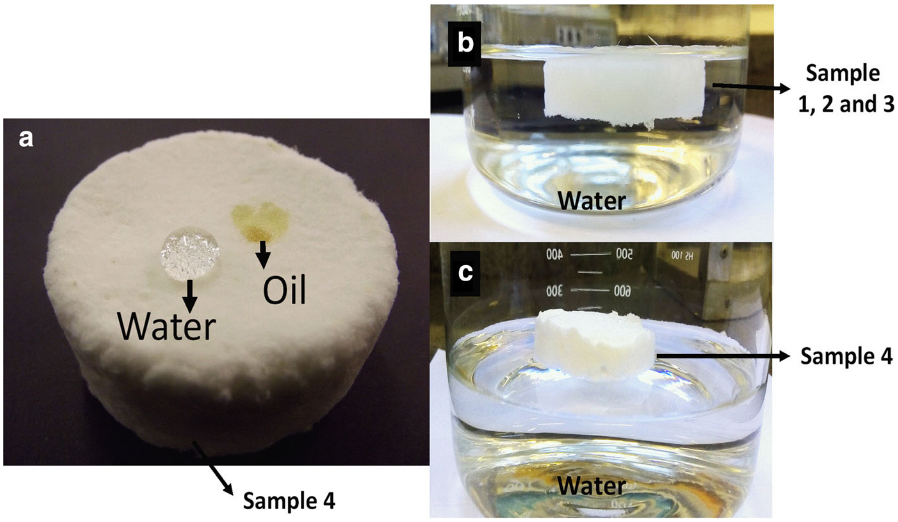

Fig. 5 Water and oil droplet on hydrophobic nanocellulose aerogel (**a**) and the behavior of the Samples 1, 2 and 3 (**b**) and Sample 4 (**c**) in water

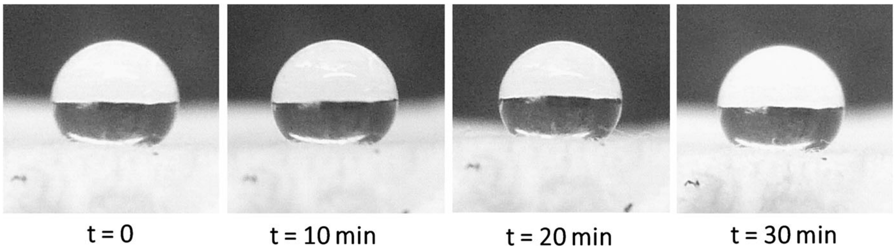

Fig. 6 Contact angle measurements for Sample 4 from $t = 0$ to $t = 30$ min

almost unchanged. This is yet another evidence of the hydrophobicity and stability of the aerogels obtained, which may be an advantage to the potential application of these materials for oil/water separation processes.

The contact angle of water with the aerogel is associated with the functionalization of the hydroxyl groups by MTMS. According to Cunha et al. (2010), the hydrophobic character of a material can be evaluated by the contact angle of a droplet of water on a surface, and when the contact angle is higher than 90°, one can classify the material as hydrophobic.

Based on these results and in combination with the FTIR analysis and the identification of bands at 1270 cm^{-1}, at 900 cm^{-1} and at 776 cm^{-1}, and the sorption tests in water medium, Sample 4 was the only one that showed hydrophobic characteristics. Because of that, the morphology and the sorption tests in oil and oil/water medium were only conducted for Sample 4, since Samples 1, 2 and 3 displayed hydrophilic tendencies.

Sorption tests in homogeneous medium (oil)

The maximum sorption capacity of Sample 4 in homogeneous oil medium was measured, in the absence of water. A maximum oil sorption capacity of 17.844 ± 1,294 g g^{-1} was obtained. Figure 7a illustrates the tests at different times up until 15 min.

The adherence of oil to the surface of aerogels occurs mainly due to the van der Waals and intramolecular interaction forces. Because of the chemical compatibility between the oil and the aerogel surface, it is possible to overcome the minimum energy required for the oil to be absorbed. In addition to that, the existence of capillary forces on the oil due to the interaction of the fiber with the oil, as well as the presence of small pores in the structure of the aerogels, are essential to provide better sorption capacity (Rengasamy et al. 2011). Also, the surface roughness plays an important role in the sorption process, avoiding the leakage of the absorbed oil (Wang et al. 2013; Wu et al. 2013).

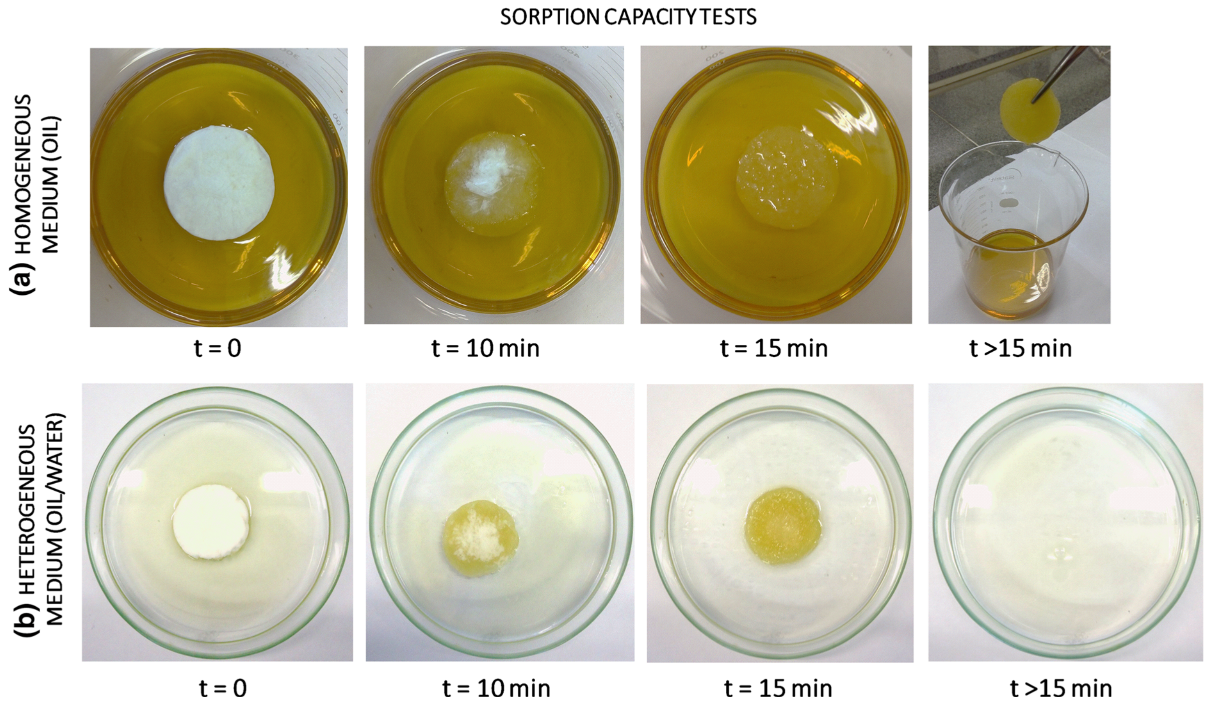

Fig. 7 Sorption capacity tests from $t = 0$ to $t = 15$ min: in homogeneous medium (oil) (**a**); in heterogeneous medium (oil/water) (**b**)

The sorption values found in this study are close to those found by Nguyen et al. (2014), who obtained a value of 18 g g^{-1} in homogeneous medium (oil) for cellulose aerogels composed by 2% cellulose dispersed in 1.9% NaOH and 10% urea.

Sorption tests in heterogeneous medium (water/oil)

Sorption tests in heterogeneous medium were performed to evaluate the absorption of oil in water by the treated aerogels. Figure 7b displays the sorption tests to different times up until 15 min. Visually, it can be observed that the aerogel in Sample 4 has a high affinity for oil, as evidenced by the little oil residue seen at $t = 15$ min. The total sorption in heterogeneous medium for Sample 4 was 16.782 ± 0.311 g g^{-1}. In these tests, the water uptake was not considered due to the fact that the values obtained for sorption in aqueous medium (0.250 g g^{-1}) were lower than those of the standard deviation calculated in the results for sorption in heterogeneous media. The efficiency of the process was calculated through the percentage of weight gained by the sample and the percent oil in water. A value of 87.9% was found. In contrast, using the vapor deposition process, Jin et al. (2015) achieved a sorption of organic solvents and oils between 12 and 22 times the aerogel weight.

Sorption processes of sorbent fibrous materials happens due to their macro and microporous structures, as well as the inter and intra-fiber interactions of the materials (Abdullah et al. 2010). According to Tansel and Pascual (2011), this process occurs in three main steps: the diffusion of the oil molecules onto the surface of the materials, the retention of the oil due to capillary forces and the accumulation of the oil into the porous structure.

According to Cervin et al. (2012), the hydrophobic coating provides the aerogel the ability to float in water, as well as the capability to absorb non-polar liquids. The depth of the chemical treatments is efficient to turn the aerogels permanently hydrophobic, evidenced by the fact that the aerogels studied kept floating on the water surface, even though not all the oil had been absorbed.

Scanning electron microscopy with field emission gun (FEG-SEM)

Figure 8 shows the micrographs of the aerogels from Sample 4. In Fig. 8a, it is possible to see the lamellar

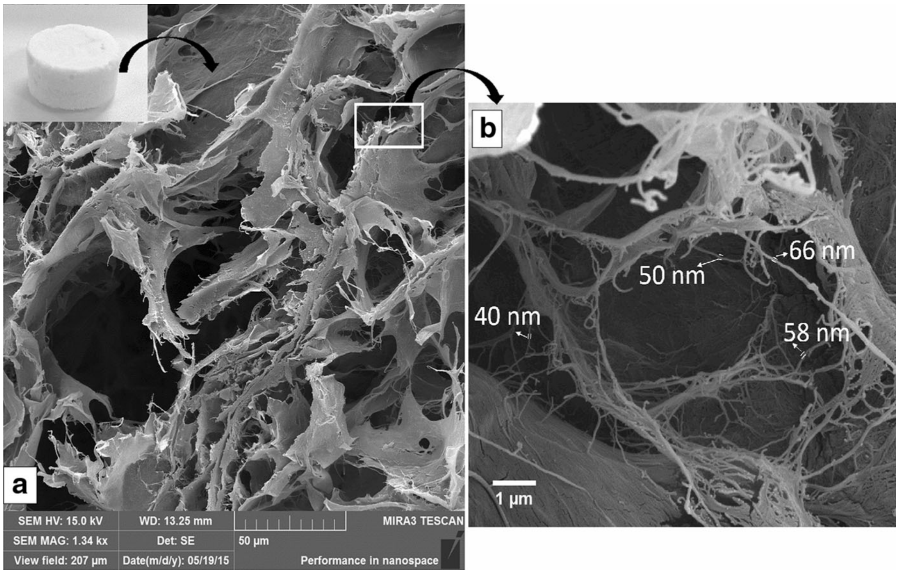

Fig. 8 FEG-SEM micrographs of Sample 4: lamellar structure (**a**) and nanofiber detail (**b**)

structure of the aerogel, which is typical of the freeze drying process, as explained in detail by Zimmermann et al. (2016). The freezing of the samples close to −80 °C prevents part of the agglomeration of the fibers. Still, fibers with diameters in the range of 40 to 66 nm were obtained (Fig. 8b), as well as a few fibers in the micrometric scale. Even though some agglomeration occurred, freeze drying can be an effective drying technique when it comes to maintaining fibers in nanoscale after drying.

Li et al. (2015) obtained CNF aerogels from freeze-drying with a rigid, entangled network of nanofibers. This provides aerogel formation with fibrillated morphology. According to Arboleda et al. (2013), in the freeze drying process, the solvent is removed by sublimation under high vacuum, and so voids similar to pores are created in the aerogel structure. The cellulose chains are joined by intra and intermolecular hydrogen bonds and van der Waals forces, forming nanofibers that have diameters in the nanometer and micrometer scale and length in micrometer scale (Pääkkö et al. 2008; Missoum et al. 2013).

Drying processes for nanocelluloses have to be chosen accordingly to avoid the densification of the samples due to the capillary tensions and due to the inter and intramolecular forces of the cellulose chains (Pour et al. 2015; Sim et al. 2015). In freeze drying, after the freezing of the samples, the nucleation and crystal growth processes take place, and after the ice has been sublimated, lamellar structure with a few nanofibers (Javadi et al. 2013; Zimmermann et al. 2016). According to Kettunen et al. (2011), freeze drying aerogels obtained from native cellulose nanofibers usually present structures that differ in pore size and micro and nanometric scale. The surface roughness provided by this process also plays an important role in its sorption efficiency, increasing the adhesion of the oil to the fiber surface, as well as increasing the surface area of the aerogels (Wang et al. 2013).

Conclusions

In the present study, freeze drying hydrophobic nanocellulose aerogels were obtained through one of four methodologies initially tested. Method 4, with 2% MTMS, mechanical stirring at 500 rpm and oven drying for 2 h at 70 °C was efficient to yield oleophilic aerogels. The mechanical fibrillation and subsequent freeze drying processes were successful, and nanostructured, lamellar aerogels were obtained. The hydrophobic aerogel absorbed up to 16 times its own weight of oil in aqueous medium, with an efficiency of approximately 88% in oil removal. As such, nanocellulose aerogels may be a viable alternative to commonly used absorbents in the removal and containment of oil spills in marine waters.

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References

Abdul Khalil HPS, Bhat AH, Yusra AFI (2012) Green composites from sustainable cellulose nanofibrils: a review. Carbohydr Polym 87:963–979. doi:10.1016/j.carbpol.2011.08.078

Abdullah MA, Rahmah AU, Man Z (2010) Physicochemical and sorption characteristics of Malaysian *Ceiba pentandra* (L.) Gaertn. as a natural oil sorbent. J Hazard Mater 177:683–691. doi:10.1016/j.jhazmat.2009.12.085

Abe K, Iwamoto S, Yano H (2007) Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. Biomacromolecules 8:3276–3278. doi:10.1021/bm700624p

Annunciado TR, Sydenstricker THD, Amico SC (2005) Experimental investigation of various vegetable fibers as sorbent materials for oil spills. Mar Pollut Bull 50:1340–1346. doi:10.1016/j.marpolbul.2005.04.043

Agência Nacional do Petróleo - ANP (2015) Brazilian statistical yearbook of petroleum, natural gas and biofuels. http://www.anp.gov.br/wwwanp/publicacoes/anuario-estatistico/2440-anuario-estatistico-2015. Accessed 18 Dec 2015

Arboleda JC, Hughes M, Lucia LA, Laine J, Ekman K, Rojas OJ (2013) Soy protein-nanocellulose composite aerogels. Cellulose 20:2417–2426. doi:10.1007/s10570-013-9993-4

Cervin NT, Aulin C, Larsson PT, Wågberg L (2012) Ultra porous nanocellulose aerogels as separation medium for mixtures of oil/water liquids. Cellulose 19:401–410. doi:10.1007/s10570-011-9629-5

Chen W, Yu H, Liu Y, Chen P, Zhang M, Hai Y (2011) Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments. Carbohydr Polym 83:1804–1811. doi:10.1016/j.carbpol.2010.10.040

Chen Z, Hu TQ, Jang HF, Grant E (2015) Modification of xylan in alkaline treated bleached hardwood kraft pulps as classified by attenuated total-internal-reflection (ATR) FTIR spectroscopy. Carbohydr Polym 127:418–426. doi:10.1016/j.carbpol.2015.03.084

Cunha AG, Freire C, Silvestre A, Neto CP, Gandini A, Belgacem MN, Chaussy D, Beneventi D (2010) Preparation of highly hydrophobic and lipophobic cellulose fibers by a straightforward gas-solid reaction. J Colloid Interface Sci 344:588–595. doi:10.1016/j.jcis.2009.12.057

De Rosa IM, Kenny JM, Maniruzzaman M, Moniruzzaman M, Monti M, Puglia D, Santulli C, Sarasini F (2011) Effect of chemical treatments on the mechanical and thermal behaviour of okra (*Abelmoschus esculentus*) fibres. Compos Sci Technol 71:246–254. doi:10.1016/j.compscitech.2010.11.023

Gavillon R, Budtova T (2008) Aerocellulose: new highly porous cellulose prepared from cellulose-NaOH aqueous solutions. Biomacromolecules 9:269–277. doi:10.1021/bm700972k

Hubbe M, Rojas OJ, Lucia L, Sain M (2008) Cellulosic nanocomposites: a review. BioResources 3:929–980. doi:10.15376/biores.3.3.929-980

Ibrahim S, Ang H-M, Wang S (2009) Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw. Bioresour Technol 100:5744–5749. doi:10.1016/j.biortech.2009.06.070

Indústria Brasileira de Árvores - IBÁ (2015) Statictics of the Brazilian tree industry. http://iba.org/images/shared/Cenarios_dezembro.pdf. Accessed 15 Dec 2015

Javadi A, Zheng Q, Payen F, Javadi A, Altin Y, Cai Z, Sabo R, Gong S (2013) Polyvinyl alcohol-cellulose nanofibrils-graphene oxide hybrid organic aerogels. ACS Appl Mater Interfaces 5:5969–5975. doi:10.1021/am400171y

Jia X, Chen Y, Shi C, Ye Y, Muhammad Abid M, Jabbar S, Wang P, Zeng X, Wu T (2014) Rheological properties of an amorphous cellulose suspension. Food Hydrocoll 39:27–33. doi:10.1016/j.foodhyd.2013.12.026

Jin C, Han S, Li J, Sun Q (2015) Fabrication of cellulose-based aerogels from waste newspaper without any pretreatment and their use for absorbents. Carbohydr Polym 123:150–1656. doi:10.1016/j.carbpol.2015.01.056

Kalia S, Boufi S, Celli A, Kango S (2014) Nanofibrillated cellulose: surface modification and potential applications. Colloid Polym Sci 292:5–31. doi:10.1007/s00396-013-3112-9

Kettunen M, Silvennoinen RJ, Houbenov N, Nykänen A, Ruokolainen J, Sainio J, Pore V, Kemell M, Ankerfors M, Lindström T, Ritala M, Ras RHA, Ikkala O (2011) Photoswitchable superabsorbency based on nanocellulose aerogels. Adv Funct Mater 21:510–517. doi:10.1002/adfm.201001431

Lavoratti A, Scienza LC, Zaterra AJ (2016) Dynamic-mechanical and thermomechanical properties of cellulose nanofiber/polyester resin composites. Carbohydr Polym 136:1–31. doi:10.1016/j.carbpol.2015.10.008

Li MC, Wu Q, Song K, Lee S, Qing Y, Wu Y (2015) Cellulose nanoparticles: structure–morphology–rheology relationships. ACS Sustain Chem Eng 3:821–832. doi:10.1021/acssuschemeng.5b00144

Likon M, Remškar M, Ducman V, Švegl F (2013) Populus seed fibers as a natural source for production of oil super absorbents. J Environ Manag 114:158–167. doi:10.1016/j.jenvman.2012.03.047

Liu F, Ma M, Zang D, Gao Z, Wang C (2014) Fabrication of superhydrophobic/ superoleophilic cotton for application in the field of water/oil separation. Carbohydr Polym 103:480–487. doi:10.1016/j.carbpol.2013.12.022

Missoum K, Belgacem MN, Bras J (2013) Nanofibrillated cellulose surface modification: a review. Materials (Basel) 6:1745–1766. doi:10.3390/ma6051745

Nakagaito A, Kondo H, Takagi H (2013) Cellulose nanofiber aerogel production and applications. J Reinf Plast Compos 32:1547–1552. doi:10.1177/0731684413494110

Nguyen ST, Feng J, Ng SK, Wong JPW, Tan VBC, Duong HM (2014) Advanced thermal insulation and absorption properties of recycled cellulose aerogels. Colloids Surf A Physicochem Eng Asp 445:128–134. doi:10.1016/j.colsurfa.2014.01.015

Ozmen N, Çetin NS, Tingaut P, Sèbe G (2007) Transesterification reaction between acetylated wood and trialkoxysilane coupling agents. J Appl Polym Sci 115:570–575. doi:10.1002/app.26069

Pääkkö M, Vapaavuori J, Silvennoinen R, Kosonen H, Ankerfors M, Lindström T, Berglundc LA, Ikkala O (2008) Long and entangled native cellulose I nanofibers allow flexible aerogels and hierarchically porous templates for functionalities. Soft Matter 4:2492–2499. doi:10.1039/B810371B

Popescu CM, Singurel G, Popescu MC, Vasile C, Argyropoulos DS, Willför S (2009) Vibrational spectroscopy and X-ray diffraction methods to establish the differences between hardwood and softwood. Carbohydr Polym 77:851–857. doi:10.1016/j.carbpol.2009.03.011

Pour G, Beauger C, Rigacci A, Budtova T (2015) Xerocellulose: lightweight, porous and hydrophobic cellulose prepared via ambient drying. J Mater Sci 50:4526–4535. doi:10.1007/s10853-015-9002-4

Rengasamy RS, Das D, Praba Karan C (2011) Study of oil sorption behavior of filled and structured fiber assemblies made from polypropylene, kapok and milkweed fibers. J Hazard Mater 186:526–532. doi:10.1016/j.jhazmat.2010.11.031

Sai H, Fu R, Xing L, Xiang J, Li Z, Li F, Zhang T (2015) Surface modification of bacterial cellulose aerogels' web-like skeleton for oil/water separation. ACS Appl Mater Interfaces 7:7373–7381. doi:10.1021/acsami.5b00846

Sim K, Ryu J, Youn HJ (2015) Structural characteristics of nanofibrillated cellulose mats: effect of preparation conditions. Fibers Polym 16:294–301. doi:10.1007/s12221-015-0294-4

Siró I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. Cellulose 17:459–494. doi:10.1007/s10570-010-9405-y

Song K, Yin Y, Salmén L, Xiao F, Jiang X (2014) Changes in the properties of wood cell walls during the transformation from sapwood to heartwood. J Mater Sci 49:1734–1742. doi:10.1007/s10853-013-7860-1

Taipale T, Österberg M, Nykänen A, Ruokolainen J, Laine J (2010) Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. Cellulose 17:1005–1020. doi:10.1007/s10570-010-9431-9

Tansel B, Pascual B (2011) Removal of emulsified fuel oils from brackish and pond water by dissolved air flotation with and without polyelectrolyte use: pilot-scale investigation for estuarine and near shore applications. Chemosphere 85:1182–1186. doi:10.1016/j.chemosphere.2011.07.006

Tarrés Q, Oliver-Ortega H, Llop M, Pèlach MA, Delgado-Aguilar M, Mutjé P (2016) Effective and simple methodology to produce nanocellulose-based aerogels for selective oil removal. Cellulose 23:3077–3088. doi:10.1007/s10570-016-1017-8

Wahi R, Chuah LA, Choong TSY, Ngaini Z, Nourouzi MM (2013) Oil removal from aqueous state by natural fibrous sorbent: an overview. Sep Purif Technol 113:51–63. doi:10.1016/j.seppur.2013.04.015

Wang J, Zheng Y, Wang A (2013) Coated kapok fiber for removal of spilled oil. Mar Pollut Bull 69:91–96. doi:10.1016/j.marpolbul.2013.01.007

Wu Z, Li C, Liang H, Chen J, Yu S (2013) Ultralight, flexible, and fire-resistant carbon nanofiber aerogels from bacterial cellulose. Angew Chem Int Ed 125:2997–3001. doi:10.1002/anie.201209676

Xie Y, Hill CAS, Xiao Z, Militz H, Mai C (2010) Silane coupling agents used for natural fiber/polymer composites: a review. Compos Part A Appl Sci Manuf 41:806–819. doi:10.1016/j.compositesa.2010.03.005

Zanini M, Lavoratti A, Zimmermann MVG, Galiotto D, Matana F, Baldasso C, Zaterra AJ (2016) Aerogel preparation from short cellulose nanofiber of the *Eucalyptus* species. J Cell Plast. doi:10.1177/0021955X16670590

Zhang Z, Sèbe G, Rentsch D, Zimmermann T, Tingaut P (2014) Ultralightweight and flexible silylated nanocellulose sponges for the selective removal of oil from water. Chem Mater 26:2659–2668. doi:10.1021/cm5004164

Zimmermann MVG, Borsoi C, Lavoratti A, Zanini M, Zaterra AJ, Santana RMS (2016) Drying techniques applied to cellulose nanofibers. J Reinf Plast Compos 35:628–643. doi:10.1177/0731684415626286