OBTAINMENT AND CHARACTERIZATION OF HYDROPHOBIC AEROGEL FROM NANOFIBERS OF UNBLEACHED CELLULOSE *EUCALYPTUS sp.*

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Abstract

Oil spills are greatly damaging to the marine wildlife, and new, environmentally friendly adsorbents are being developed to minimize these spills. In this context, cellulose - a natural, nontoxic and biodegradable material - is a promising material for obtaining hydrophobic adsorbent materials. This work aims to develop nanocellulose aerogels from cellulose nanofiber (CNF) suspensions obtained by mechanical fibrillation. CNF suspensions were freeze dried and chemically treated with triethoxyvinylsilane (VTES) through vapor deposition. Oil adsorption tests and contact angle measurements were made. The treated aerogels presented a contact angle with water of 130 °, and oil adsorption in aqueous medium of 24 times its own weight.

Key words: Cellulose nanofibers, Aerogel, Hydrophobicity.

Theme Area: Environmental technologies

1 Introduction

The consumption and production of petroleum products are increasing. In 2013, Brazil produced 2.1 million oil barrels per day, occupying the 8th place in world production. According to Environmental Accident Report data 2012, IBAMA, in Brazil about 635,000 liters of oil were spilled during the process of exploration and transport, causing environmental damage.

To choose the most appropriate technique to remove the water oil from water factors such as cost, effectiveness and availability of the material are evaluated. Natural fibers are promising materials for this application to be obtained from renewable sources and present excellent oil adsorption capacity when subjected to appropriate chemical treatment (WAHI *et al.*, 2013).

The cellulose nanofibers are obtained mostly by mechanical means in which an aqueous suspension of cellulose fibers is ground into smaller fibrils. The nanofibers may be used in the formation of adsorbent material from this suspension, called aerogel, with potential to be used in permeation processes and adsorption of gases and liquids (AALTONEN & JAUHIAINEN, 2009; SEHAQUI *et al.*, 2011). Aerogels are materials highly porous with low density, they are formed from the replacement of the liquid present in the gel by a gas, without collapse of its structure. To promote the extraction of this liquid it must be submitted to a drying process such as freeze-drying or supercritical drying. These methods are important because they prevent the collapse of the structure due to surface tension and capillary pressure formed between the water and the network of fibers (JAVADI *et al.*, 2013).

To make the surface of aerogel hydrophobic is necessary to carry out a functionalization of hydroxyl groups in the surface of the material, which can be realized by the vapor deposition silanes technique (JAVADI *et al.*, 2013).

In this study was used unbleached pulp, the species *Eucalyptus sp*., for aerogel formation. The surface treatment of the aerogel was made by vapor deposition with vinyl-triethoxy-silane silane (VTES). The aerogel were characterized by adsorption experiments in homogeneous and heterogeneous media, contact angle measurement and field emission scanning electric microscopy (FEG-SEM) to visualize the structure obtained and the presence of cellulose nanofibers.

2 Materials and Methods

2.1 Materials

The materials used in this study were: unbleached pulp species Eucalyptus sp, provided by Klabin / RS, vinyl triethoxy silane (VTES) form Sigma Aldrich and SAE 20W50 motor oil from Ipiranga Petrochemical.

2.2 Methods

2.2.1 Aerogel Preparation

To obtain the cellulose nanofiber suspension, the cellulose plate was dispersed in distilled water in a concentration 3% by mass. After this process, the solution was grinding in a stone mill (Masuko - Sangyo MKCA6-2J) with recirculation, for 5 hours. The obtained suspension was packaged in cylindrical molds. The samples, made in triplicate, were frozen at -80 ° C, with liquid nitrogen, and transferred to the freeze-drying (L101- Lio Top), where they remained for 72 hours.

After freeze-drying, the surface of the aerogel was treated by vapor deposition with VTES. The obtained aerogels were placed in glass vials containing a becker with 1 ml of VTES, in each container. A screen was placed over the becker to support the aerogel. After the containers were closed and kept for 48 hours at 70 °C in an oven. At the end of that period, to remove the VTES excess, the aerogels remained for 3 hours in a vacuum oven with pressure 0.03 mbar, according methodology adapted from Nguyen *et al.* (2014).

2.2.2 Aerogel Characterization

The quickly homogeneous adsorption test (oil) were performed as adaptation of F726-12 standard.

For contact angle measurements were analyzed the samples before and after chemical treatment with silane. They were placed on a glass slide and, with a syringe, was added a drop of distilled water at three points across the sample. It was recorded the image with a digital camera every 5 minutes, for a period of 30 minutes. The images were analyzed by Surftens software.

The heterogeneous adsorption test (oil and water) was performed with the amount of oil absorbed in the quickly adsorption test, using the same mass of oil adsorbed in this assay. In a Petri dish with 200 ml of distilled water was added the estimated quantity of oil. The aerogels were placed in the middle for 15 ± 0.3 min. The aerogel was removed from the middle with a clip in a vertical orientation, leaving it drain for 60 ± 2 seconds and then weighed, as methodology established by Zhang *et al.* (2013). The test were performed in triplicate and the amount of adsorbed oil is given by Equation 1.

$$CA = \frac{m_f - m_i}{m_i} \quad (1)$$

where:

CA= adsorption capability (g/g)
m_i = initial weight (g)
m_f = end weight (g)

The morphological analyses was performed in a field emission scanning electric microscopy (FEG Mira 3 - Tescan) to visualize the fiber diameter and aerogel structure.

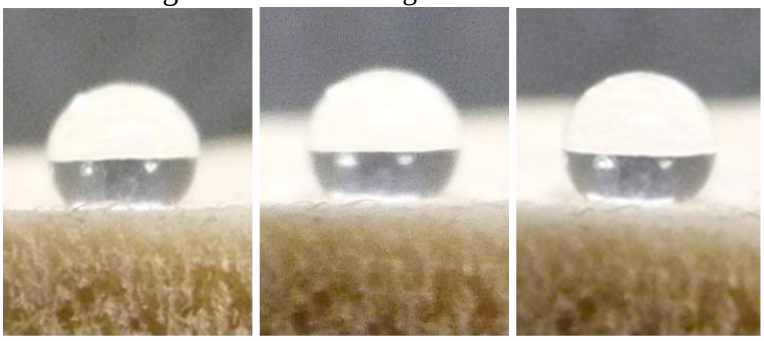
3 Results and discution

3.1 Contact angle

The hydrophobic character of the aerogel was determined by measuring the contact angle of its surface with water. In the assay with the aerogel without silane treatment it could not be measured due to the immediately water adsorption. The contact angle for the samples treated with silane was 130.21 ± 1,02º, as shown in Figure 1.

The water droples were kept over the sample during 30 minutes, until the endo of the analyses they maintained the initial contact angles, as well as their geometric forms, without been adsorbed by the aerogel, demonstrating the hydrophobicity property.

Figure 1 – Contact angle characterization.



t = 0 min t = 15 min t = 30 min

The contact angle of water with the aerogel is associated with the functionalization of the hydroxyl groups by VTES. Reactive silanol groups are physically adsorbed by hydroxyl groups of cellulose though hydrogen bonds. These groups also react with each other to form Si-O-Si and Si-OC bonds, promoting the hydrophobization of the aerogel surface (XIE *et al.*, 2010).

3.2 Homogeneous adsorption test (oil)

The figure 2 illustrates the steps of homogeneous adsorption test. The aerogel adsorbed 26.38 ± 0.509 grams of oil by gram of sample.

Figure 2 – Steps of homogeneous test.

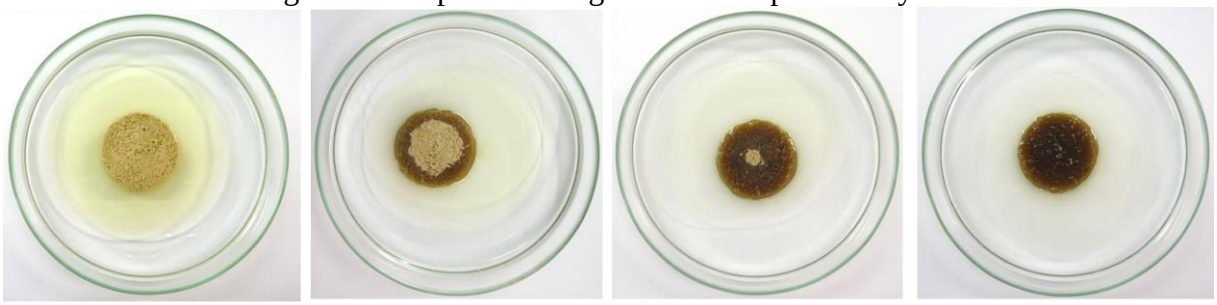
t = 0 t = 5 min t = 10 min t = 15 min

Nguyen et al. (2014) in the study with aerogel with 2% of short unbleached cellulose fibers dispersed in 1.9 % sodium hydroxide and 10 % of urea, obtained adsorption of 17.6 grams of oil by gram of sample, in homogeneous adsorption test with oil.

3.3 Heterogeneous adsorption analyses (water / oil)

Figure 3 shows the steps of heterogeneous adsorption analyses. The aerogel adsorbed 23.948 ± 0.285 grams of oil by gram of sample, with efficiency in oil removal, adsorbing 90.76% of oil present in the middle. The hydrophobic aerogel showed oleophilic and hydrophobic properties with good selectivity been able to remove the oil present on the water surface.

Figure 3 – Steps of heterogeneous adsorption analyses.

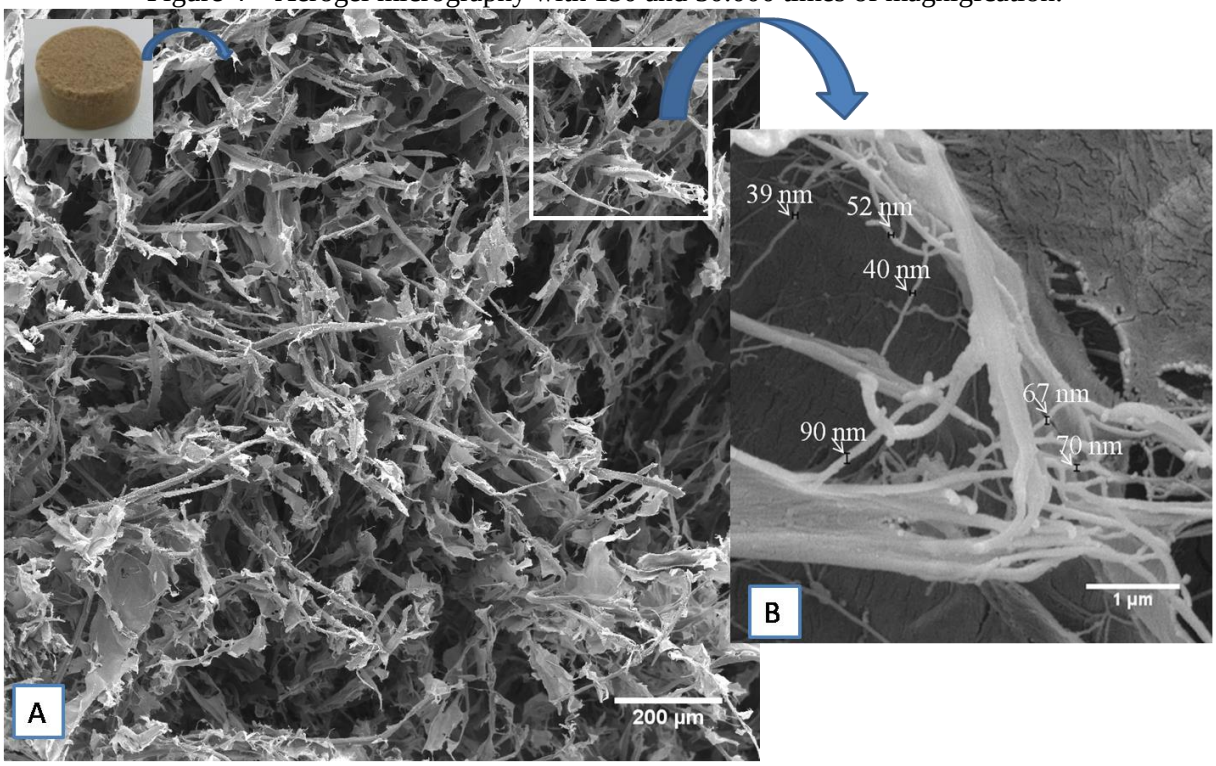


According to Cervin *et al.* (2012) hydrophobic aerogel coating provides to aerogel hydrophobic characteristics that made its floating on the water without adsorbing it and capability to adsorbing non-polar liquids. The superficial treatment was depth enough to make the aerogels permanently hydrophobic it can be evidenced by the fact that the aerogel remains floating on the water even if all the oil has been adsorbed (AULIN *et al.*, 2010; CERVIN *et al.*, 2012).

3.4 Scanning Electron Microscopy

Figure 4 shows the micrographs of aerogels with original magnification 150 times (a) and 50.000 times (b). It is possible to visualize the presence of fibers with diameter in nanometer scale and lamellar structure with pore formation.

Figure 4 – Aerogel micrography with 150 and 50.000 times of magnigfcation.



During the freezing process nucleation it was observed the nucleation and growth of ice crystals, the ice formed was sublimated. In the freeze-drying process providing the

formation of pores and lamellar structure (JAVADI *et al.*, 2013). According Kettunen *et al.* (2014), aerogel from native cellulose nanofibers obtained by freeze-drying has irregular structures with different pore sizes in micrometer and nanometer scale.

The entangled cellulose nanofiber provide aerogel formation with fibrillar morphology and strong molecular interactions. The cellulose chains are joined by intra and intermolecular hydrogen bonds and van der Walls forces, forming nanofibers that have diameters in the nanometer and micrometer scale and length in micrometer scale, composed by the aggregation of 10 – 50 elementary fibrils (PÄÄKKÖ *et al.*, 2007; MISSOUM *et al*., 2013).

4 Conclusion

The mechanical milling process was effective for obtaining cellulose fiber suspension in nanometer scale. The freezing and freeze drying of the suspension yielded the formation of pores and lamellar structure to aerogel. The chemical treatment, by silane vapor deposition, gave hydrophobicity to the adsorbent. The aerogel had oil sorption capacity, in aqueous media, 24 times its own weight, with 90.76% efficiency in removing the oil, thereby it has potential to be used as oil adsorbent in an aqueous medium.

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