

Analysis of Compression Resistance and Oil Adsorption Capacity of Cellulose/NaOH Cryogels

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Abstract: This work aimed at analyzing the petroleum adsorption capacity and the compressive strength of cellulose cryogels produced with the addition of 4 and 8% (w/w) sodium hydroxide (NaOH). Cryogels were produced from a 1.5% (m/m) suspension of cellulose microfibrils, which originated from *Pinus elliotti*, in distilled water. The addition of NaOH increased the compression strength of cryogel by 30% when compared to cryogel without the reagent. Due to the 50% decrease in volume, the cryogel FLNB-8h (8% NaOH) has its petroleum adsorption capacity decreased in average by 58%, whereas the FLNB-4 (4% NaOH) cryogel had it only by 14%. The cellulose suspension which provided the best results for the properties of the cryogels tested had a 4% concentration of NaOH.

Keywords: Cryogel; cellulose; NaOH; adsorption; compression resistance

1 Introduction

Petroleum is one of the most important energy sources for humans. Nevertheless, accidents involving the spilling of petroleum and its derivatives often occur during the process of using it, resulting in loss of energy as well as in threats to the environment. Oil accidents, such as the one from 2010 on the Deepwater Horizon¹ platform, during which there was an explosion followed by a fire that resulted in the leakage of 5 million barrels of petroleum, cause significant environmental damage, therefore underscoring the importance of oil spill prevention and cleanup should be emphasized [1].

Some procedures can be adopted for the remediation of these accidents, such as barriers and skimmers, chemical dispersants, in situ burning, bioremediation, use of oleophilic adsorbents, among others. Cryogels are a class of materials that can be used as adsorbents. They are characterized by their highly porous structure, which gives the material low specific mass and high surface area. They can be produced from different materials, such as silica, alumina, rubber and cellulose derivatives [2].

The production of cellulose cryogels can be considered interesting because cellulose is the most abundant natural polymer in the environment, thus, being widely used in industry. However, for its better use, the major challenge to be overcome is the disadvantage of these cellulosic cryogels when compared to other cryogels, since the first ones have lower mechanical properties [3]. The process of mercerization (which consists in the addition of NaOH to the cellulose fibers) improves softness, strength and elongation of the fibers with a variety of chemicals, which also increase the dimensional stability of the fibers [4].

¹ Available in: <<http://www.greenpeace.org/brasil/pt/Noticias/Pior-vazamento-de-petroleo-completa-cinco-anos/>>. Access in: March 29, 2017.

Hence, the objective of the present work was to add sodium hydroxide to the cellulose cryogel, and to evaluate the compressive strength and oil adsorption capacity of the final product.

2 Experimental

2.1 Materials

The cellulose used in the present work, which was the unbleached long fiber (FLNB) of the species *Pinus elliotti*, was supplied by Trombini (Fraiburgo-SC). Sodium hydroxide (NaOH) P.A. was purchased from Neon Commercial, and crude oil was supplied by the Alberto Pasqualini Refinery (Canoas-RS).

2.2 Cryogel Production

A suspension was made with distilled water and the FLNB at a cellulose concentration of 1.5% (w/w). This suspension was placed in a Masuko Sangyo micronizer-model MKCA6-2J (Japan) to perform the grinding of the fibers and the disintegration of those for 5 hours. The suspension was centrifuged and the supernatant was separated from it. 4 and 8% (w/w) of NaOH (FLNB-4H and FLNB-8H, respectively) were added to the supernatant. These were kept under mechanical stirring until complete dissolution of the reagent. The supernatant and precipitate mixture were held in a thermostated bath with hydro-alcoholic solution at -11 °C for 2 hours with mechanical stirring at 1000 rpm. At the end of the mixing, approximately 50 g of the suspension was placed in a beaker and left in the oven at 70 °C for 24 hours for gel formation. After the gelation process, the formed gels were placed into beakers containing water, the water was changed several times, until all excess of NaOH was removed. The method used for the addition of NaOH was based on the method used by Gavillon [4]. After the chemical treatment, each sample was packed in a cylindrical cast. Samples were frozen in a Panasonic-PRO MDF Series ultra-freezer at -80 °C, and then taken to a vacuum chamber for sublimation of the ice. The process was carried out in a Lio Top lyophilizer - Model L101 (Brazil).

2.3 Specific Mass and Porosity

The cryogel specific mass was characterized the mass of the sample divided by its volume, and its porosity was calculated by the Eq. (1).

$$\text{Porosity (\%)} = \left(1 - \frac{\rho_{\text{cryogel}}}{\rho_{\text{cellulose}}}\right) \quad (1)$$

Thus, being, ρ_{cryogel} the specific mass of the cryogel ($\text{g}\cdot\text{cm}^{-3}$), and $\rho_{\text{cellulose}}$ the specific mass of the cellulose² ($0.533 \text{ g}\cdot\text{cm}^{-3}$).

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analyzes were performed on a Nicolet IS10 Thermo Scientific (USA) spectrophotometer. Each spectrum was obtained by 32 scans, which had the wave number ranging from 4000 cm^{-1} to 400 cm^{-1} , and presented a resolution of 4 cm^{-1} using a diamond-attenuated total reflection (ATR).

2.4 X-ray Diffraction and Crystallinity Index

X-ray diffraction (XRD) is one of the main techniques of microstructural characterization of crystalline materials. The analysis was performed using a Shimadzu XRD-6000 diffractometer (Japan). The analyzed strip was from $2\theta = 2^\circ$ to 30° , with step of 0.05° , and time of integration of 2 s. The crystallinity of the cellulose was calculated using the following Equation (2). This method was based on the research carried out by Peng et al. [5].

$$\text{CrI} = \left(\frac{I_{200} - I_{am}}{I_{200}}\right) \times 100 \quad (2)$$

² Cellulose was received in the form of cardboard. The specific mass of the cellulose was measured from the mass and volume of a sample.

where, CrI is the crystallinity index (%); I_{200} is the value of the maximum intensity of the peak of the plane (2 0 0), which is located at $2\theta \sim 22.5^\circ$ angle of diffraction; I_{am} is the valley intensity between the peaks corresponding to the planes (2 0 0) and (1 1 1), at $2\theta \sim 18^\circ$ angle of diffraction.

2.5 Compression Tests

The compressive strength tests were performed on a Q800 AT DMA equipment, TA Instruments (USA), with a parallel plate compression clamp. The samples were cut into cubes of 1 cm^3 , and the compression ratio started at of 3 N.min^{-1} , reaching the maximum force of 18 N due to the equipment limit. The assay was performed in triplicate.

2.6 Adsorption Capacity in Homogeneous and Heterogeneous Media

In order to evaluate the petroleum adsorption capacity of the cryogels, adsorption tests were carried out in homogeneous (petroleum or water) and heterogeneous (petroleum and water) media, in accordance with the F726-12 standard of the American Society of Testing and Materials [6]. The cryogels were previously weighed and placed in a vessel containing sufficient petroleum/water so they could float freely. After 15 minutes, they were removed and suspended for 30 seconds to remove excess liquid, and weighed again. The adsorption capacity (C_{ads}) was calculated with Eq. (3).

$$C_{ads} = \frac{m_f - m_o}{m_o} \quad (3)$$

where m_o and m_f (g) are the mass of the cryogel before and after the test.

3 Results and Discussion

3.1 Specific Mass and Porosity

The nomenclature, volume, specific mass and porosity of the cryogels are shown in Tab. 1.

Table 1: Nomenclature, volume (cm^3), specific mass (g.cm^{-3}) and porosity (%) of cryogel

Cryogel	NaOH concentration (%)	Volume (cm^3)	Specific mass (g.cm^{-3})	Porosity (%)
FLNB	0	22,645	$0,017 \pm 0,001$	$96,86 \pm 0,14$
FLNB-4H	4	21,675	$0,053 \pm 0,008$	$90,87 \pm 1,57$
FLNB-8H	8	10,752	$0,049 \pm 0,005$	$90,64 \pm 0,95$

The structure of the cryogel is directly related to the size and the distribution of the ice crystals which are formed during the freezing of the cellulose suspension. In this case, the addition of sodium hydroxide promoted the swelling of the cellulose fibers. This swelling, caused the agglomeration and retraction of the cryogel three-dimensional structure, which resulted in a decrease in the porosity of the cryogels when compared to the treated cryogel, and in increase in their specific mass.

The results obtained for specific mass and porosity ranged from 0.017 to 0.053 g.cm^{-3} and from 90.64 to 96.86% respectively, as shown in Tab. 1. The values found in the present work were similar to those found by Nguyen et al. [7], who found density of 0.040 g.cm^{-3} , and porosity of 94.8% for aerogel with addition of 1.9% NaOH and 10% urea. Zanini et al. [8] obtained 0.0644 g.cm^{-3} and 91% for aerogel with 2% NaOH addition, results which were much lower than the found results found by Gavillon and Butnova [9], who obtained density of 0.14 g.cm^{-3} , and porosity of 96% with the addition of 7.6% NaOH.

Fig. 1 shows the cryogels FLNB, FLNB-4H and FLNB-8H in top, side and cross-sectional views.

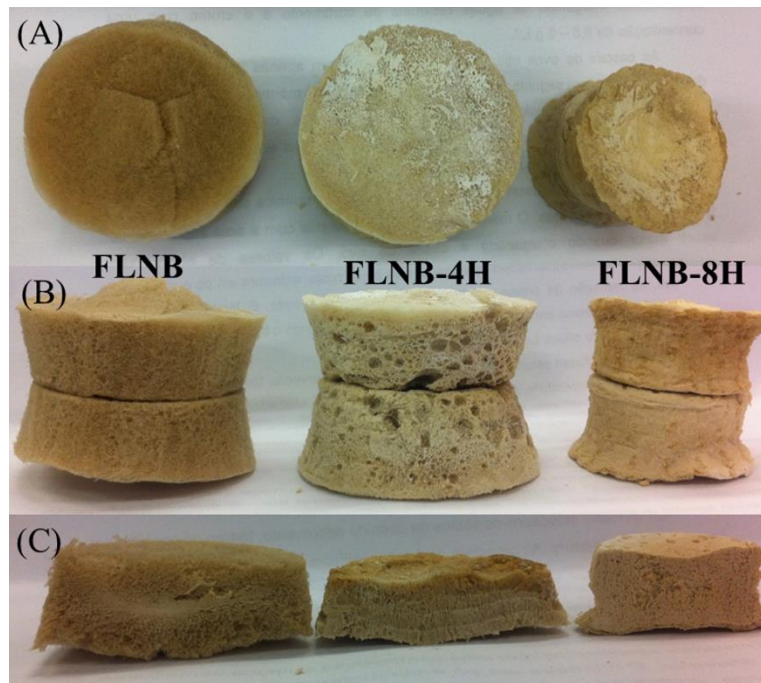


Figure 1: Photograph of cryogels FLNB, FLNB-4 and FLNB-8 in (A) top view, (B) side view and (C) cross section

Analyzing the photographs shown in Fig. 1, one can see that by increasing the NaOH concentration there is a greater compactness of the cryogels when compared to the sample without addition of the alkali. The cryogel FLNB-8H had a decrease of approximately 50% in its volume (as shown in Tab. 1), making the cryogel structure less porous than the others. The cryogel diameter was 41.7 ± 0.3 mm for FLNB, 42.7 ± 0.8 mm for FLNB.4H, and 30.6 ± 0.7 mm for FLNB-8H, that is, there was a 30% decrease in the diameter of the FLBN-8H cryogel.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 2 shows the FTIR spectra obtained from the cryogels after the chemical treatment with NaOH being, compared to the untreated sample (FLNB). The assignments of the bands are presented in Tab. 2.

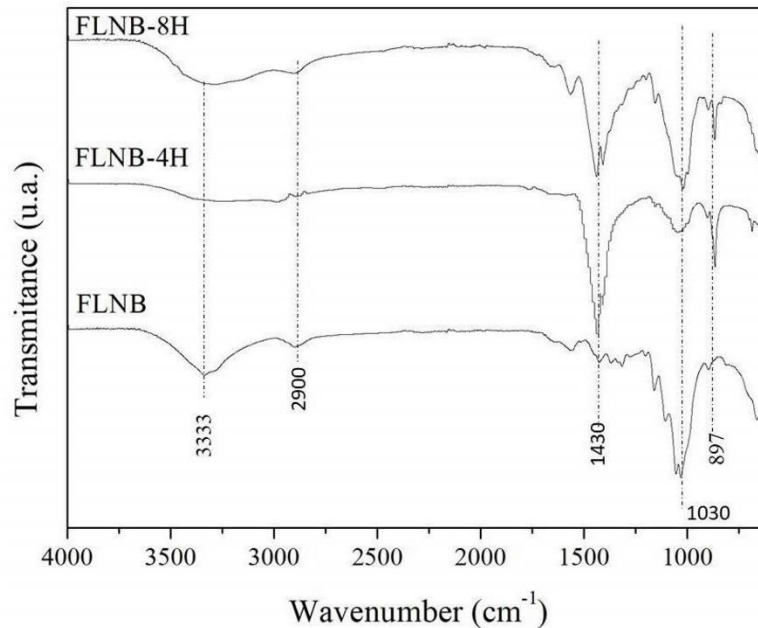


Figure 2: FTIR spectra of the FLNB, FLNB-4H, FLNB-8H cryogels

Caption: FLNB (cryogel without treatment); FLNB-4H (cryogel with addition of 4.0% (w/w) NaOH) and FLNB-8H (cryogel with addition of 8.0% (w/w) NaOH).

Table 2: Assignment of the FLNB, FLNB-4H and FLNB-8H cryogels FTIR bands. (Source: 8, 10, 11, 12, 13, 14)

Wavenumber (cm ⁻¹)	Assignment
3700-3000	ν_{O-H}
2900	ν_{C-H}
1430 (1550-1280)	ν_{CH_2}
1030 (1190-920)	δ_{C-O} C ₆ of cellulose
897	δ_{C-H}

Note: ν = stretching and δ = deformation.

According to Oh et al. [13], the decrease in the intensity of the stretching band of the CH₂ bond at 1430 cm⁻¹ is caused by the mercerization process (NaOH treatment) of the cellulose. This can be seen, according to Dinand et al. [10], in the displacement of the CH bond deformation band at 897 cm⁻¹ and the increase in band intensity, in which there was the conversion of Cellulose I to Cellulose II, due to the mercerization process.

3.3 Compression Tests, X-ray Diffraction and Crystallinity Index

Tab. 3 shows the values found for the compression strength test for a 50% deformation of the specimen for the FLNB, FLNB-4H and FLNB-8H cryogels.

Table 3: Compressive strength with 50% deformation of the specimen

Cryogel	Compression strength (kPa)	Crystallinity index (%)
FLNB	74.17 ± 0.48	75.0
FLNB-4H	95.41 ± 2.92	74.5
FLNB-8H	50.64 ± 1.67	61.5

Caption: FLNB (cryogel without treatment); FLNB-4H (cryogel with addition of 4.0% (w/w) NaOH), and FLNB-8H (cryogel with addition of 8.0% (w/w) NaOH).

According to the values shown in Tab. 3, cryogel FLNB-4H has a compressive strength 28% higher than cryogel FLNB and 88% higher than cryogel FLNB-8H. According to Gavillon [4], treating the fibers with an alkaline solution, such as NaOH, causes the fiber to swell to various extents, depending on the type and concentration of the alkali, as well as on the temperature. This process increases the strength and elongation of the fibers, also increasing the dimensional stability of the fibers.

The decrease in the compressive strength of the FLNB-8H cryogel can be explained by the decrease in crystallinity, as shown in Fig. 3. The FLNB-4H cryogel presented the same cellulose I characteristic peaks at 2θ angles of approximately 14.7° (1 -1 0), 16° (1 1 0), 20° (1 0 2), 22.3° (2 0 0) and 34° (0 0 4). The mercerization is responsible for inducing the irreversible transformation of the native cellulose crystal structure or cellulose I into cellulose II [4]. The diffraction pattern of FLNB-8H showed the presence of two peaks which corresponded to cellulose II diffraction at 2θ angles of approximately 11° (1 -1 0) and 20° (1 1 0). These results show that mercerization actually occurred in this cryogel [16].

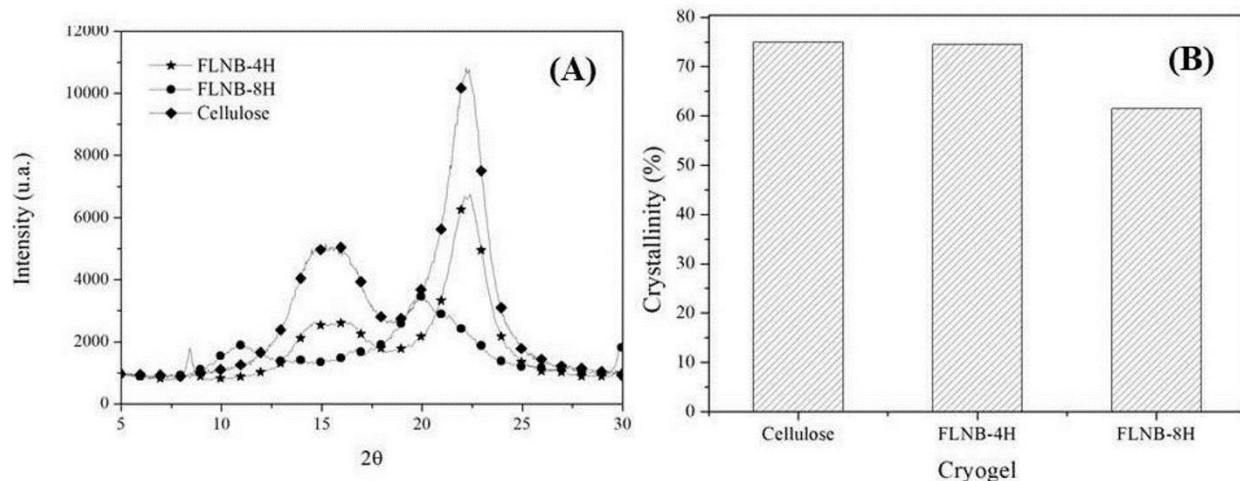


Figure 3: (A) DRX Spectra and (B) Crystallinity of the fibers of the FLNB-4H and FLNB-8H cryogels and the source cellulose

In addition to the increase in alkaline concentration, the bond strength of the crystal is overcome by hydration of the Na^+ ion, causing irreversible swelling in the fibers. At the same time, the intensity of the inter- and intra-hydrogenic cellulose bonds decrease with increasing amorphous areas, which leads to a loss of crystallinity (Fig. 3(B)) [15].

3.4 Adsorption capacity in homogeneous and heterogeneous media

Adsorption tests were carried out to evaluate the adsorption capacity of the studied cryogels. Fig. 4 shows the comparison of results obtained from homogeneous and heterogeneous media adsorption tests.

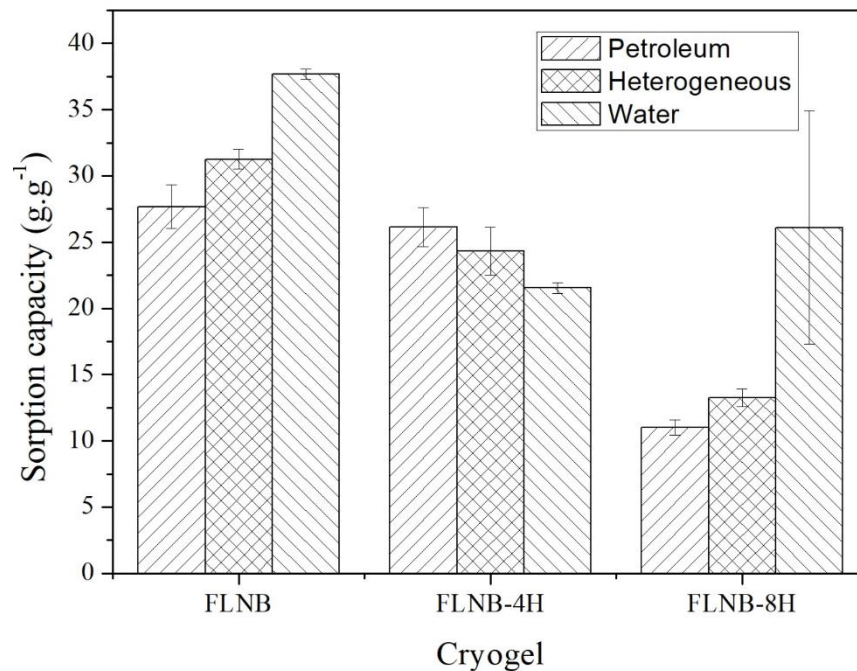


Figure 4: Adsorption capacity of the cryogs

Caption: FLNB (cryogel without treatment); FLNB-4H (cryogel with addition of 4.0% (w/w) NaOH) and FLNB-8H (cryogel with addition of 8.0% (w/w) NaOH).

Based on the data presented in the graph in Fig. 4, the addition of NaOH to the cellulose suspension decreased the adsorption capacity of the FLNB-4H, and the FLNB-8H cryogels if compared to the untreated cryogel (FLNB). NaOH changes the cryogel structure, compacting the fibers and decreasing their porosity. The decrease in adsorption is a result of the decrease in the porosity of the cryogels due to the addition of NaOH.

There was a decrease in the adsorption capacity of 16% (31.24 to 26.11 g.g⁻¹) and 12% (27.68 to 24.21 g.g⁻¹) for the FLNB-4H in the homogeneous and heterogeneous media respectively. The water adsorption capacity of the FLNB-4D cryogel decreased more than 16 g.g⁻¹ when compared to the FLNB cryogel. For the FLNB-8H the decrease was considerably higher, reaching 65% (31.24 for 11.01 g.g⁻¹) for the homogeneous media and 52% (27.68 for 13.25 g.g⁻¹) for the heterogeneous media. These decreases in adsorption capacities are due to the lower porosity of these cryogels when compared to the FLNB cryogel.

The adsorption capacity of the cryogels studied in this work was higher than that found by other authors who used different materials, such as polypropylene fibers (10 g.g⁻¹) [17]. It was similar to those found using polyurethane foam (PU) modified with MnO₂ nanowires (4-36 g.g⁻¹), depended on the oils or solvents [18], and cotton (30 g.g⁻¹) [19].

4 Conclusions

In the mercerization process, the concentration of 4 and 8% NaOH was added to the cellulose suspension in order to increase the mechanical resistance of the cryogel. The cryogel FLNB-4H showed the highest

compressive strength (95.41 kPa), as well as the highest heterogeneous adsorption capacity (24.21 g.g⁻¹) when compared to the untreated (FLNB) cryogel and to the one with 8% of NaOH (FLNB-8H).

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References

1. Lin, J., Shang, Y., Ding, B., Yang, J., Yu, J. et al. (2012). Nanoporous polystyrene fibers for oil spill cleanup. *Marine Pollution Bulletin*, 64, 347-352.
2. Du, A., Zhou, B., Zhang, Z., Shen, J. (2013). A special material or a new state of matter: a review and reconsideration of the aerogel. *Materials*, 6, 941-968.
3. Zhang, J., Cao, Y., Feng, J., Wu, P. (2012). Graphene-oxide-sheet-induced gelation of cellulose and promoted mechanical properties of composite aerogels. *Journal of Physical Chemistry*, 116, 8063-8068.
4. Gavillon, R. (2007). *Preparation and characterization of ultra porous cellulosic materials*. École Nationale Supérieure des Mines de Paris.
5. Peng, Y., Gardner, D. J., Han, Y., Kiziltas, A., Cai, Z. et al. (2013). Influence of drying method on the material properties of nanocellulose I: thermostability and crystallinity. *Cellulose*, 20, 2379-2392.
6. ASTM. F726-12: Standard test methods for sorbent performance of adsorbents. Philadelphia, 2012.
7. Nguyen, S. T., Feng, J., Kai Ng, S., Wong, J. P. W., Tan, V. B. C. et al. (2014). Advanced thermal insulation and absorption properties of recycled cellulose aerogels. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 445, 128-134.
8. Zanini, M., Lavoratti, A., Lazzari, L. K., Galiotto, D., Pagnocelli, M. et al. (2017). Producing aerogels from silanized cellulose nanofiber suspension. *Cellulose*, 24, 769-779.
9. Gavillon, R., Budtova, T. (2008). Aerocellulose: new highly porous cellulose prepared from cellulose-NaOH aqueous solutions. *Biomacromolecules*, 9, 269-277.
10. Dinand, E., Vignon, M., Chanzy, H., Heux, L. (2002). Mercerization of primary wall cellulose and its implication for the conversion of cellulose I to cellulose II. *Cellulose*, 9, 7-18.
11. Fu, J., Wang, S., He, C., Lu, Z., Huang, J. et al. (2016). Facilitated fabrication of high strength silica aerogels using cellulose nanofibrils as scaffold. *Carbohydrate Polymers*, 147, 89-96.
12. Lee, J. A., Yoon, M. J., Lee, E. S., Lim, D. Y., Kim, K. Y. (2014). Preparation and characterization of cellulose nanofibers (CNFs) from microcrystalline cellulose (MCC) and CNF/Polyamide 6 composites. *Macromolecular Research*, 22, 738-745.
13. Oh, S. Y., Yoo, D. I., Shin, Y., Kim, H. C., Kim, H. Y. et al. (2005). Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. *Carbohydrate Research*, 340, 2376-2391.
14. Xiao, S., Gao, R., Lu, Y., Li, J., Sun, Q. (2015). Fabrication and characterization of nanofibrillated cellulose and its aerogels from natural pine needles. *Carbohydrate Polymers*, 119, 202-209.
15. Jiao, C., & Xiong, J. (2014). Accessibility and morphology of cellulose fibres treated with sodium hydroxide. *Bioresources*, 9, 6504-6513.
16. Novo, L. P., Bras, J., García, A., Belgacem, N., Curvelo, A. A. (2015). Subcritical water: a method for green production of cellulose nanocrystals. *ACS Sustainable Chemistry & Engineering*, 3, 2839-2846.
17. Wu, D., Fang, L., Qin, Y., Wu, W., Mao, C. et al. (2014). Oil sorbents with high sorption capacity, oil/water selectivity and reusability for oil spill cleanup. *Marine Pollution Bulletin*, 84, 263-267.
18. Zhang, T., Kong, L., Dai, Y., Yue, X., Rong, J. et al. (2017). Enhanced oils and organic solvents absorption by polyurethane foams composites modified with MnO₂ nanowires. *Chemical Engineering Journal*, 309, 7-14.
19. Singh, V., Kendall, R. J., Hake, K., Ramkumar, S. (2013). Crude oil sorption by raw cotton. *Industrial & Engineering Chemistry Research*, 52, 6277-6281.