Production of Nanocellulose from Waste Cellulose

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Nanocellulose obtained from waste cellulose has a promising wide range of opportunities to obtain the superior material properties towards various end-products. Here, we report on waste cellulose material from used diapers subjected to an acid hydrolysis using sulfuric acid to obtain nanocellulose. The prepared nanocellulose was further characterized with the aid of different techniques to elucidate crystallinity (85% degree), purity and morphology of the obtained product.

1. Introduction

Cellulose is a biopolymer found naturally in plant cells such as wood and cotton. It is the most abundant polymer in nature and the main constituent in the cell wall of trees and plants. The study of its chemical structure and physical-chemical characteristics has paved the way for its use in a wide range of applications. Despite being the most available natural polymer on earth, it is only quite recently that cellulose has gained importance as a nanostructured material, mainly in the form of nanocrystalline cellulose and micro/nanofibrillar cellulose.

Nanocellulose is a natural, renewable, biodegradable and biocompatible material that has high strength and elastic modulus, high surface area, high aspect ratio, chemical functionality, dimensional stability, moisture absorption properties and thermal stability. Large-scale production of nanocellulose, with a high reduction of energy consumption, has recently become possible using various, but still expensive, physical (Harmsen et al., 2010), chemical (Klemm et al., 2005) and enzymatic (Klemm et al., 2005) pre-treatment methods to obtain fibers from hemicellulose and lignin. On the other hand, the production of nanocellulose in a convenient and environmental-friendly way, from abundant waste materials (e.g. cellulose from used diapers and incontinence products) is still a challenge.

Here, we report for the first time the production of nanocellulose from the waste cellulose material deriving from used diapers and incontinence products. To obtain the nanocellulose, a chemical approach (Rånby, 1951), consisting of a controlled hydrolysis using sulfuric acid solutions (Favier et al., 1995; Beck-Candanedo et al., 2005; Elazzouzi-Hafraoui et al., 2008), was used. A comprehensive characterization, including X-ray diffraction (XRD), FT-IR spectroscopy, thermogravimetric analysis (TG-DTG), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy – Energy dispersive X-ray spectroscopy (TEM-EDS) of the obtained nanocellulose, was also performed.

This paper demonstrates the possibility to recover cellulose from waste diapers, obtaining a material with a potential high added value.

2. Experimental section

2.1 Materials

Waste cellulose from recycled diapers and incontinence products was used as received. All procured reagents were of analytical grade and used without additional purification steps. Sodium hydroxide pellets (NaOH), sodium chlorite ($NaClO_2$), glacial acetic acid (CH_3CO_2H) and sulphuric acid (H_2SO_4) were received from Sigma-Aldrich. All experimental solutions were prepared using de-ionized (DI) water.

2.2 Preparation of nanocellulose

Since cellulose of diapers is already purified from non-cellulosic (hemicellulose, lignin) material, the first step was a bleaching using sodium chlorite ($NaClO_2$). This step was performed in an experimental apparatus using a magnetically stirred three necked flask (Sarno et al., 2014; Sarno and Ponticorvo, 2018). In particular, 5 g of dried pre-treated fibers were heated to 80 °C for 5 hours with constant stirring in a mixture made up of equal parts (1:1/v:v) of a solution composed of acetate buffer (27 g of NaOH and 75 mL of glacial acetic acid, diluted to 1 L in distilled water) and aqueous sodium chlorite (1.7 wt.% $NaClO_2$ in water). Then, it was washed and centrifuged several times with DI water and adjusted to a neutral pH. The centrifuged material was dried at 80°C for a day. Bleached cellulose was then added to 10 ml of concentrated sulphuric acid and 20 ml of DI water, heated at 40°C with constant stirring for an hour to obtain a well-mixed solution. It was then washed several times with the water adjusted to a neutral pH. The prepared suspended solution was centrifuged at 7,500 rpm for 30 min. The produced nanocellulose was dried at 80°C in order to obtain a nanocrystalline powder.
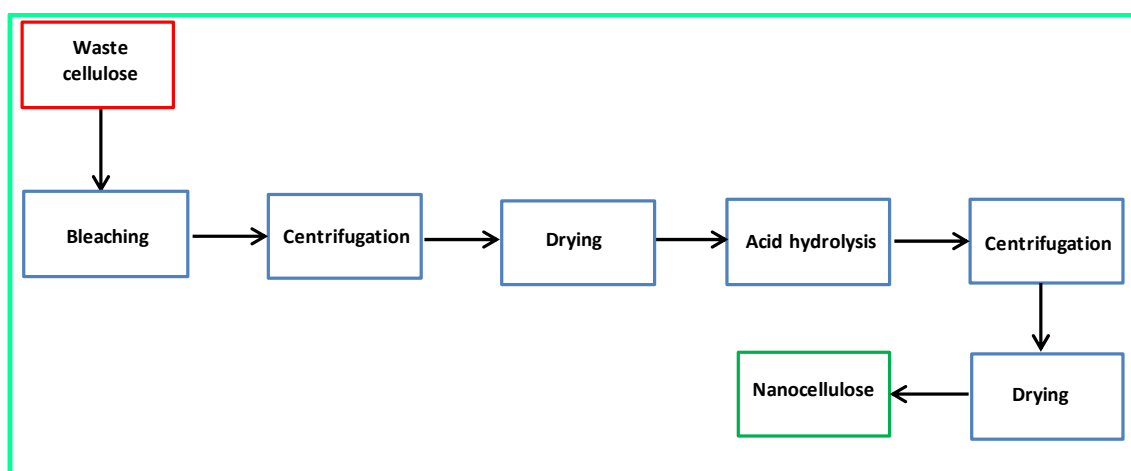

Figure 1: Scheme of different steps for the preparation of nanocellulose

2.3 Characterization of nanocellulose

The obtained nanocellulose was characterized by numerous techniques. XRD measurements were performed with a Bruker D8 AdvanceX-ray diffractometer using CuK_α radiation. The samples were scanned in 2ϑ range of 5–90°. The KBr technique was applied for determining the FT-IR spectra of the samples by using Vertex 70 apparatus (Bruker Corporation). Spectra were recorded at a scanning range from 4000 to 400 cm^{-1}.

Thermal analysis (TG–DTG) in air flow was performed with a Thermogravimetric Analyser SDTQ 600 TA Instruments, at a 10 K/min heating rate. Scanning electron microscopy images were collected with a FESEM LEO 1525 microscope. TEM images were acquired using a FEI Tecnai electron microscope, operating at 200 kV with a LaB_6 filament as the source of electrons, equipped with an energy dispersive X-ray spectroscopy (EDX) probe. For the preparation of the TEM sample, drops of nanocellulose suspension in water were deposited on carbon-coated electron microscope grids.

3. Results and discussion

Generally, cellulose includes a crystalline and an amorphous phases. In order to study the crystallinity of the produced nanocellulose, XRD analysis was carried out. The X-ray diffraction patterns of the starting waste cellulose and the obtained nanocellulose are shown in Figure 2. The main peaks from XRD pattern of nanocellulose are at 2θ values of: 14.7°; 16°; a well-defined main peak around 22°; and 35°, which correlate, respectively, with the (1 $\overline{1}$ 0), (1 1 0), (2 0 0) and (0 4 0) crystal lattice planes. These peaks can be assigned to the typical cellulose I crystalline structure (Borysiak and Doczekalska, 2005; Shimazaki, 2007; Sullivan et al., 2015). This confirms that the crystalline nanocellulose was mainly the crystalline structure of cellulose I. It also confirmed that the obtained nanocellulose is very similar to the starting material, which spectrum is conditioned by the presence of the impurities of the starting sample. The high intensity and sharpness of the (2 0 0) diffraction peak at 2θ=22° is indicative of a high degree-of-order and of a high perfection of the crystal lattice (Teixeira et al., 2011).
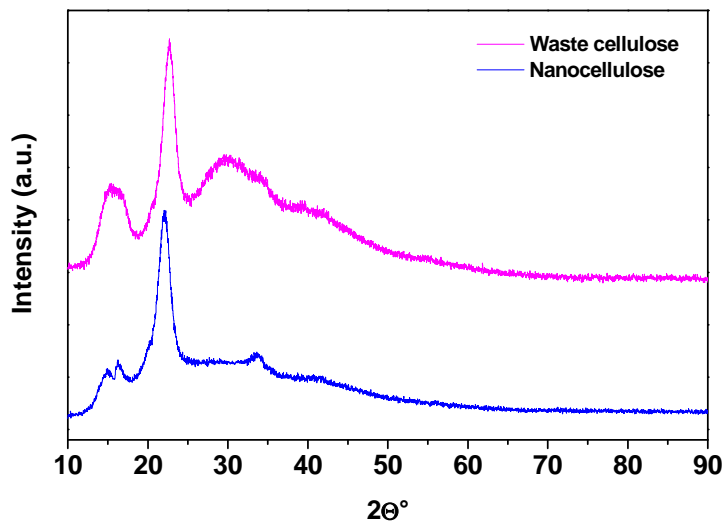
Figure 2: Comparison of XRD patterns of waste cellulose (magenta line) and obtained nanocellulose (blue line)
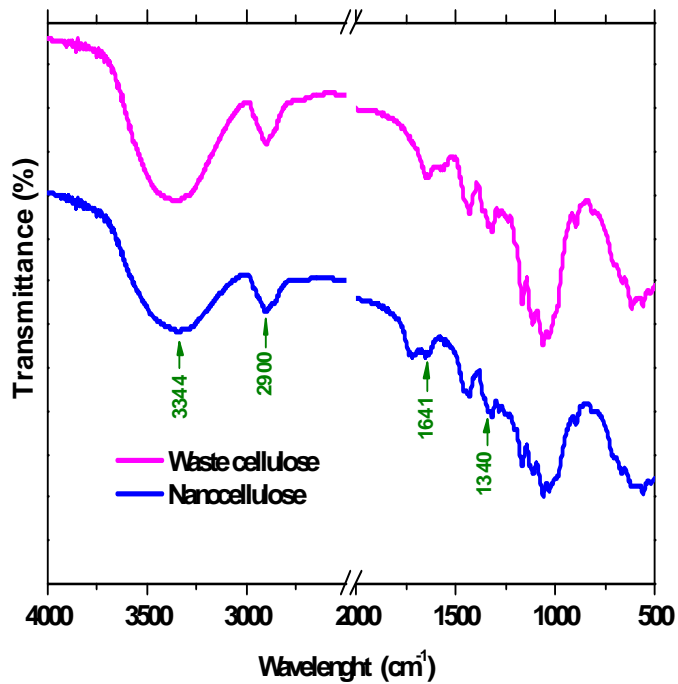

Figure 3: Comparison of FTIR spectra of waste cellulose (magenta line) and obtained nanocellulose (blue line)

The crystallinity index (CI) of the cellulose was calculated using the following equation (Segal et al., 1959) Eq. (1):

$$CI(\%) = \frac{(I_{002} - I_{AM})}{I_{002}} * 100 \qquad (1)$$

in which, I_{002} is the maximum intensity of (0 0 2) diffraction line and I_{AM} is the intensity of the amorphous fraction.

The calculated crystallinity index for waste cellulose is about 68% while the crystallinity index for nanocellulose is about 85%. These results indicate that the treatments have increased the order of the macromolecule packages due to the decrease in the ratio of the amorphous parts of the cellulose.

Infrared spectroscopy that works based on the atoms' vibrations in a molecule was carried out. When the test molecule absorbs infrared radiation, the chemical bonds in it vibrate and is able to stretch, contract or bend. The FTIR spectra of waste cellulose and nanocellulose are shown in Figure 3.

The absorption peaks at 3344 cm^{-1} and around 2900 cm^{-1} were attributed to the O-H (Li et al., 2014) and C-H (Khalil et al., 2010) stretching vibrations, respectively. The peak absorption at 1641 cm^{-1} was reported as the O-H vibration of absorbed water (Mandal and Chakrabarty, 2011). In addition, the peak for C-H and C-O vibrations contained in the polysaccharide rings of cellulose is around 1340 cm^{-1} (Nacos et al., 2006). Alkali treatment reduces hydrogen bonding by removal of the hydroxyl groups through a reaction with sodium hydroxide. This led to the increase in –OH concentration, which is evident from the increased intensity of the peak in the range 3300–3500 cm^{-1} in the nanocellulose sample, compared to waste cellulose. The peak centered at 1725 cm^{-1} can be ascribed to residual pectin. Finally, the peaks observed in the spectra between the 1013 and 1160 cm^{-1} range are due to the C–O–C pyranose ring (antisymmetric in phase ring) stretching vibration (Alemdar and Sain, 2008; Mandal and Chakrabarty, 2011; Li et al., 2012). The region in the range 800-1500 cm^{-1} is a unique fingerprint region for cellulose where the majority of peaks in that range are found also for nanocellulose sample, indicating that, regardless of acid treatment, cellulose maintained a similar chemical structure to the original untreated specie.
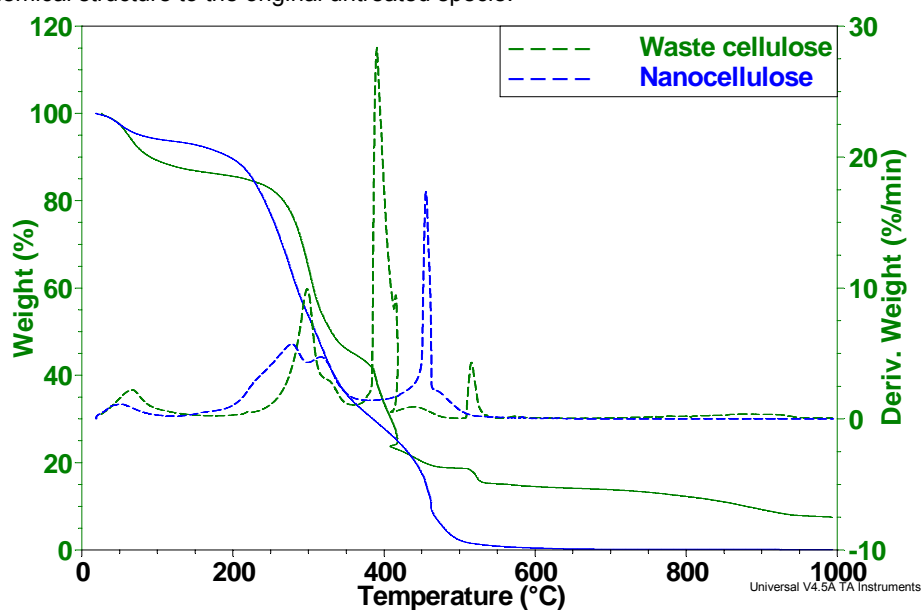

Figure 4: TG-DTG profiles of waste cellulose (blue line) and of the obtained nanocellulose (green line) in air flow

The thermal conversions, in air flow, in a temperature range 25-1000°C of both waste cellulose and nanocellulose are shown in Figure 4. The first weight loss, which occurred below 150°C for both samples, is related to the release of moisture and absorbed water. Three domains can be clearly identified in the TG profile of waste cellulose: (i) decomposition of cellulose in the temperature range 210-370°C (maximum weight loss at 296°C) (Yang et al., 2007); (ii) decomposition of sodium polyacrylate polymer (SAP-superadsorbent), residue of the cellulose separation from waste diapers, centered at 410°C); (iii) second weight loss of cellulose decomposition centered at 440 °C. The residue, equal to ~8 wt%, and the weight loss at 530 °C are also due to SAP. This evaluation was supported by the thermal analysis, not shown here, of the pure cellulose and SAP used for the preparation of diapers.

The nanocellulose thermal stability is lower than that of the waste cellulose. This reduction of thermal stability may be attributed to the introduction of the negatively charged sulfate half ester groups and a larger number of free ends of chains in nanocellulose caused by the sulfuric acid hydrolysis, as observed by different authors (Roman and Winter, 2004; Wang et al., 2007; Teixeira et al., 2010; Correa et al., 2010; Mariano et al., 2016). The TG profile, in this case is consistent with pure cellulose. The lack of residue in the nanocellulose sample confirms the removal of impurities.
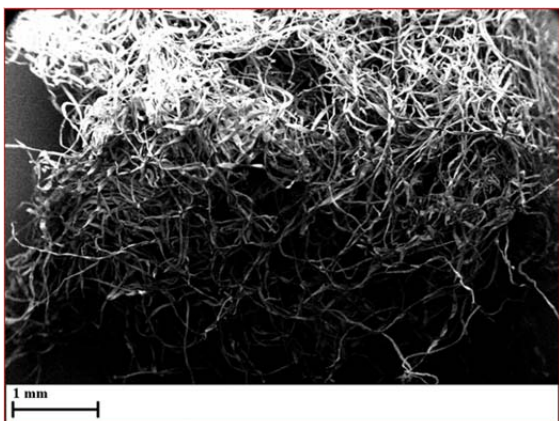
Figure 5: SEM image of waste cellulose

Morphological changes between the waste cellulose and the obtained nanocellulose can be observed in Figure 5 and Figure 6. A SEM image of starting waste cellulose is depicted in Figure 5. It shows cellulose fibers length of several millimeters.

A transmission electron micrograph obtained from a dilute suspension of nanocellulose is presented in Figure 6. The suspension is constituted of individual cellulose fragments consisting of rods. These fragments have a length ranging from 150 nm up to 300 nm, and an average diameter ranging from 8 to 13 nm. The average aspect ratio (L/d, L being the length and d the diameter) of these rods is therefore around 19-23.
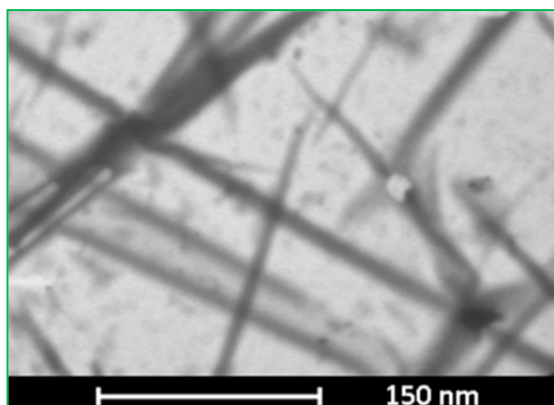

Figure 6: TEM image of nanocellulose

These results prove that regenerated nanocellulose can be derived from waste diapers to be used as highly added value nanoadditive for coatings and in biomedical, sensors, energy, nanocomposites applications.

4. Conclusions

Nanocellulose was successfully obtained for the first time from waste cellulose from used diapers and characterized with numerous techniques (XRD analyses, FT-IR spectroscopy, Scanning Electron Microscopy, Trasmission Electron Microscopy, TG-DTG analysis). The obtained nanocellulose shows a good level of purity and high crystallinities. The crystallinity index for the obtained nanocellulose is 85%. The result proves that the obtained waste cellulose can be used to produce nanocellulose which can be utilized for a large number of applications.

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