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A novel green approach for the preparation of cellulose nanowhiskers from white coir

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ABSTRACT

The aim of this work was to optimize the extraction of cellulose nanowhiskers (CNW) from unripe coconut husk fibers (CHF). The CHF was delignified using organosolv process, followed by alkaline bleaching (5% (w/w) H_2O_2 + 4% (w/w) NaOH; 50 °C, 90 min). The CHF was subsequently hydrolyzed with 30% (v/v) sulfuric acid (60 °C, 360 min). The process yielded a partially delignified acetosolv cellulose pulp and acetic black liquor, from which the lignin was recovered. The CNW from the acetosolv pulp exhibited an average length of 172 ± 88 nm and a diameter of 8 ± 3 nm, (aspect ratio of 22 ± 8). The surface charge of the CNW was −33 mV, indicating a stable aqueous colloidal suspension. The nanocrystals presented physical characteristics close to those extracted from cellulose pulp made by CHF chlorine-pulping. This approach offers the additional advantage of extracting the lignin as an alternative to eradication.

1. Introduction

Cellulose nanowhiskers (CNW), sometimes referred to as whiskers, are structures in nanoscale dimensions with a wide range of applications in different fields. Key applications of these structures involve their use as support systems for synthesis of metallic nanoparticles (Xiong, Lu, Zhang, Zhou, & Zhang, 2013), intelligent or active packages (Azeredo, Miranda, Rosa, Nascimento, & De Moura, 2012), and engineered nanocomposites (Eichhorn et al., 2010). CNW can replace carbon nanotubes as fillers because of their relatively low cost of production, easy obtainment process, low density (about 1.566 g/cm^3), non-abrasive nature, biocompatibility, and biodegradability (Postek et al., 2011).

Several sources of CNW like wood, non-wood fibers, algae, tunicates, and bacterial cellulose have been reported (Eichhorn et al., 2010). However, unripe coconut husk fiber (CHF) represents an exceptional major source of cellulose for the extraction of the CNW because it is significantly abundant, low-cost, and is an underutilized byproduct produced in several tropical regions (Rosa et al., 2010).

It has already been reported that CNW from CHF possess diameters smaller than 5 nm and an aspect ratio of 39 ± 14 (Rosa et al., 2010). In the work of Rosa et al. (2010), CHF were subjected to a series of treatments involving: (i) washing with hot water, (ii) bleaching with sodium chlorite ($NaClO_2$), (iii) pre-hydrolysis with nitric acid (HNO_3), and (iv) acidic hydrolysis with sulfuric acid (H_2SO_4, 64% (w/w)). Although it was possible to obtain a stable colloidal suspension, it presented a dark-brown aspect, which limited its use as filler in nanocomposites for films and packages, mainly owing to the presence of residual lignin (Rosa et al., 2010). Another limitation of this approach in pulping was the use of the chloro-based compound, $NaClO_2$, which is known to be detrimental to the

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environment owing to its role in the formation of organochlorine byproducts.

Usually, the higher the lignin content in a fiber, the higher the amount of reagents required to remove it and allow access to cellulose in order to produce CNW. However, lignin can be extracted as a separate product from CHF, using approaches that are closer to green chemistry and biorefinery principles (Ng, Tay, & Ng, 2013).

The aim of this work was to optimize the experimental conditions for the extraction of CNW from CHF, with a view to extracting cellulose and lignin through a chlorine-free pulping approach that allows for minimizing the waste of lignin, while using easily recoverable and low-environmental impact reagents. The physical and chemical properties of CNW were evaluated by analysis of surface charge, crystallinity index, crystal size dimension, FTIR spectroscopy, and thermogravimetric analysis. These results were compared to the already existing methods to produce CNW from CHF.

2. Methods

2.1. Material

Unripe coconut husk fiber (CHF) was collected as a city waste in Fortaleza, Ceará State, Brazil, and processed in a pilot plant processing unit from where it was transported to Embrapa Tropical Agroindustry (CNPAT), also in Fortaleza. The raw CHF was ground in Wilye mill (FORTINOX – STAR FT 80) with a 1.0 mm sieve. All solvents and reagents were of analytical grade and were used as received without any modification. The reagents 97% (w/w) NaOH, 37% (w/w) HCl, 30% (w/w) H_2O_2, 99.7% (w/w) acetic acid (AcOH), and 98% (w/w) H_2SO_4 were obtained from Vetec Química Fina Ltda – Duque de Caxias, RJ, Brazil, while 80% (w/w) $NaClO_2$ was obtained from Sigma–Aldrich, Saint Louis, MO, USA.

2.2. Acetosolv pulping (AP)

The CHF fibers were cooked in a mixture of 93% (w/w) AcOH and 0.3% (w/w) HCl in a hydrothermal reactor at 110 °C, in a ratio of 1:10 (w/v fiber:solution) with constant stirring for 180 min. At the end of the reaction, the mixture was separated into solid (acetosolv pulp) and liquid fractions (black liquor). The acetosolv pulp (AP) was washed with fresh AcOH (80 °C) to prevent lignin redeposition on the fiber. The black liquor (BL) was stored for further separation of the recovered lignin (RL) (Benar & Schuchardt, 1994).

2.3. Generation of recovered lignin (RL)

The BL was concentrated in a rotary evaporator (BUCHI – R-210/215) to recover the acetic acid. After this step, the volume of BL was diluted 10 times with distilled water at 80 °C to precipitate the lignin. The RL was filtered and washed with distilled water at 25 °C until it reached a pH close to the washing water. Subsequently, it was dried in a vacuum desiccator with silica gel.

2.4. Alkaline-peroxide bleaching (APB)

The AP was bleached with a solution of 5% (w/w) H_2O_2 and 4% (w/v) NaOH in a beaker at 50 °C in a ratio of 1:20 (fiber:solution, w/v) with constant stirring for 90 min. At the end of the reaction, the bleached acetosolv pulp (BAP) was vacuum-filtered and washed with distilled water until it reached the pH of water used in the washing step. The BAP was oven-dried at 50 °C for 24 h, and then the bleaching procedure was repeated.

2.5. Extraction of cellulose nanowhiskers (CNW)

The final BAP was stirred in a 30% (v/v) (43.6%, w/w or 8 mol/L) solution of H_2SO_4 at 60 °C, in a 1:8.75 (w/v) ratio of fiber:solution for 360 min (Wang, Cao, & Zhang, 2006). At the end of the process, the reaction was halted by adding 10 times the volume of cold deionized water (~10 °C). The colloidal suspension was centrifuged in three cycles of 13,000 rpm (26,400 × g) (HITACHI – CR 22GIII) for 15 min until the supernatant began to turn turbid. In other words, in the first and in the second centrifugations, the supernatant was clear, and the CNW were in the bottom; in the third centrifugation, the supernatant began to become turbid, indicating that the CNW were beginning to leak to the supernatant. Between each centrifugation, the suspension was ultra-sonicated (UNIQUE – Cell Disruptor – 500 W) at 90% power for 5 min to prevent the formation of agglomerates. Thereafter, the suspension was dialyzed with tap water for 24 h until it reached a pH of 6–7. The suspension was ultra-sonicated at the end of the dialyses as described previously, prior to characterization.

2.6. Characterization

2.6.1. Chemical characterization of fibers

The CHF, AP, and BAP fibers were chemically analyzed. The moisture, extractive, and Klason lignin contents were determined in accordance to TAPPI T 421 om-02 (2002), TAPPI T 204 cm-97 (1997), and TAPPI T 222 om-22 respectively (2000). Hemicellulose and alpha-cellulose contents were analyzed as described by Yokoyama, Kadla, and Chang (2002) and TAPPI T 203cm-99 (2009). The results are presented in dry weight of fibers.

2.6.2. FTIR analysis

Samples of CHF, AP, BAP, and RL were ground and pelletized using KBr (1:50, w/w). The spectra were recorded in the range of 4000 cm^{-1} to 400 cm^{-1} (Agilent Cary 640 FTIR) using Fourier transformation.

2.6.3. Electron microscopy

The three different fibers (CHF, AP, and BAP) were analyzed by scanning electronic microscopy (SEM). All fibers were metalized (Emitech K550) with gold sputtering prior to examination and scanned at an acceleration voltage of 15 kV (Zeiss DSM 940A).

The CNW were measured by transmission electronic microscopy (TEM). A volume of 1 mL of nanocellulose 5% (w/v) suspension was dropped onto a Formvar^{TM}/Carbon support with a 300 mesh copper grid. After 2 min, the excessive water was drained with a Whatmann paper no.2, and the grid was inverted and allowed to touch a drop of 2% (w/v) uranyl acetate for 5 min. This process was repeated three times, and the grid was air-dried at room temperature for 24 h. The grids were examined in a JEOL JEM 1200FxII microscope. The length and width of 100 crystals were recorded using the software GNU Image Manipulation Program (GIMP 2.8).

2.6.4. X-ray diffractogram

Samples of CHF, AP, BAP, and dried CNW were analyzed in an Xpert MPD diffractometer with Co tube in 40 kV and 40 mA in the 2θ range from 3° to 50°. The crystallinity index (CI) was calculated as the ratio between the integrated area of all crystalline peaks and the integrated total area (Rabek, 1980). The diffractogram peak deconvolution was performed with the Gausian function of the software PeakFit® of Systat Software Inc (SigmaPlot^{TM}), using the following equation:

$$\mathrm{CI}\,(\%) = \frac{I_C}{I_C + I_A} \qquad (1)$$