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Cellulose nanocrystals from acacia bark–Influence of solvent extraction

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ABSTRACT

The isolation of cellulose nanocrystals from different lignocellulosic materials has shown increased interest in academic and technological research. These materials have excellent mechanical properties and can be used as nanofillers for polymer composites as well as transparent films for various applications. In this work, cellulose isolation was performed following an environmental friendly procedure without chlorine. Cellulose nanocrystals were isolated from the exhausted acacia bark (after the industrial process of extracting tannin) with the objective of evaluating the effect of the solvent extraction steps on the characteristics of cellulose and cellulose nanocrystals. It was also assessed the effect of acid hydrolysis time on the thermal stability, morphology and size of the nanocrystals, through TGA, TEM and light scattering analyses. It was concluded that the extraction step with solvents was important in the isolation of cellulose, but irrelevant in the isolation of cellulose nanocrystals. Light scattering experiments indicated that 30 min of hydrolysis was long enough for the isolation of cellulose nanocrystals.

1. Introduction

In recent years, there has been a growing interest in the study of sustainable raw materials which present potential use in nanotechnology. In this sense, cellulose nanocrystals (CNC) derived from plant fibers have attracted interest as new materials mainly for polymer reinforcement. The major components of plant fibers are cellulose (40–50%), hemicellulose (20–30%) and lignin (10–18%) [1]. Besides these components, variable amounts of solvent extractable compounds and inorganic molecules are also found.

Obtaining cellulose nanocrystals from various types of lignocellulosic arrays involves a series of processes that may start with solvent extraction steps using solvents of different polarities or solvent mixtures to remove extractives [2–4]. This is a high cost and time-consuming step. Chemically, extractives in wood are components of low molecular weight. They include a wide range of substances such as flavonoids, lignans, stilbenes, tannins, inorganic salts, fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, terpenes, starch, glycosides, saponins, and essential oils [5]. Water-soluble wood extractives mainly consist of organic salts, sugars, some polysaccharides and phenolic substances [6]. The composition and amount of the extractives depend on factors such as wood species, wood age and the location of the wood in the tree [5]. Bark is the part of the plant where the soluble substances are mainly present [6].

Following solvent extraction, lignin and hemicellulose are selectively removed from the fiber in the pulping step [7]. The most commonly used process involves heating with alkaline solutions. In general, after this step, the pulp still shows dark color and needs the use of bleaching processes to achieve greater level of brightness [8]. Conventional bleaching processes involve the use of chemicals based on chlorine (chlorine, chlorine dioxide, sodium hypochlorite), usually in a series of steps depending on the desired degree of whiteness. The major drawback of these processes is the formation of toxic organic compounds, mainly dioxins. Because of this, new Totally Chlorine Free (TCF) bleaching sequences have been developed, which are mainly based on oxygen, hydrogen peroxide and ozone [7].

Once cellulose is isolated from the plant, CNC can be obtained by acid hydrolysis under controlled conditions [9]. The amorphous regions are destroyed, leaving intact the crystalline segments. Depending on the sources of the starting cellulose and on the

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extraction process, various sizes of nanocrystals can be obtained. CNC consist of needle-shaped nanoparticles with high crystallinity, high surface area, average length of 100–200 nm and diameter in the range of 5–10 nm [10]. The aspect ratio, defined as the ratio between length and diameter, extends over a wide range [11]. Crystallinity may vary from 65 to 95%, giving high strength, rigidity and modulus, close to the theoretical modulus of perfect crystals [2]. The morphology and properties of CNC depend not only on the source of the starting cellulose, but also on the extraction process and on the characterization technique used [9]. Among the sources used to obtain CNC we can quote cotton [12], curauá [13], byproducts such as rice husk [3] and maize straw [4], marine plants [14] and still bacterial sources [15]. As main fields of applications of the CNCs, we can mention reinforcing fillers in polymers [14,16,17], packaging [18,19], biomedics [20,21] and water treatment [22,23].

The exhausted bark of *Acacia mearnsii* (black acacia) obtained after tannin extraction was the raw material used in this work. Black acacia is one of the most important cultivated trees in the state of Rio Grande do Sul, Brazil. This kind of acacia is of wide industrial use and it provides various products used as raw materials in industry. Plant extracts rich in tannin and phenols, as well as flocculants used in water treatment processes, filtering pharmaceutical and chemical products are obtained from its bark [24]. Nowadays, the bark residue remaining after tannin extraction leads to an environmental problem being generally burned. According to the Brazilian Institute of Geography and Statistics (IBGE) [25] the production of black acacia bark was around 70.000 ton in 2014 and this amount was totally produced in the state of Rio Grande do Sul, where the climate is adequate for growing this plant. Thus, the use of exhausted black acacia bark to produce CNC can be an interesting alternative to give value and to help solving an environmental problem caused by the tannin industry.

This study aimed to isolate and to characterize CNC from exhausted acacia bark following two different experimental procedures – with and without solvent extraction – to evaluate the importance of this step on the morphology and thermal stability of the materials.

2. Experimental

2.1. Materials

Exhausted acacia bark was supplied by SETA S.A. (Estância Velha/RS, Brazil). Hexane (Fmaia, Brazil), ethanol (Fmaia, Brazil), sodium hydroxide (Labsynth, Brazil), hydrogen peroxide (CAQ Química, Brazil), nitric acid (Fmaia, Brazil), acetic acid (CAQ Química, Brazil) and tetra-acetylethylenediamine (TAED, activator) (Acros Organics, New Jersey, USA) were used as received. All solvents and reagents were of analytical grade.

2.2. Procedures

2.2.1. Isolation of cellulose

Cellulose isolation procedures were based on Rosa et al. and Rehman et al. [3,4]. The dried acacia bark was milled under liquid nitrogen and sieved (35 mesh). Part of the powder was dewaxed using a sequence of hexane/ethanol/water in a Soxhlet apparatus (6 h each step). Both the dewaxed and the non-dewaxed bark particles were delignificated at 121 °C, in autoclave (Stermax 20EHD), using a 5% aqueous NaOH solution with a 1:30 bark to liquor ratio (g/mL), for 30 min. Then, they were washed with deionized water to neutral pH. In the sequence, two bleaching processes were followed. In the first one, the bark was treated with an aqueous solution of H_2O_2 (2%) and TAED (0.2%), at pH 12, for 12 h, at 48 °C (liquor to pulp ratio 25 mL:1 g). After this step, the materials were washed with deionized water to neutral pH. The second bleaching step was the treatment of 150 mg pulp with 5.0 mL of 80% acetic acid (v/v) and 0.5 mL of 70% nitric acid (v/v), at 120 °C, for 15 min. The residual materials were washed with ethanol 95%, and deionized water to neutral pH. They were finally dried at 60 °C to constant weight. Samples prepared using the solvent extraction step were named SE (samples with Solvent Extraction) and samples prepared without the step of solvent extraction were named WSE (samples Without Solvent Extraction).

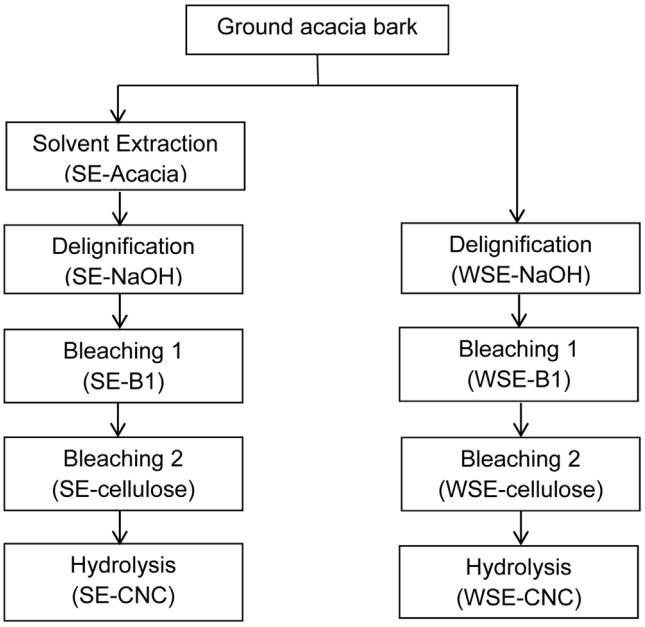

Fig. 1. Scheme to obtain cellulose nanocrystals (CNC).

2.2.2. Preparation of cellulose nanocrystals (CNC)

The SE-cellulose and WSE-cellulose were mixed with sulfuric acid 64% (w/w) at a ratio of 1:8.75 (g/mL), at 45 °C. Different hydrolysis times were tested: 15, 30, 60, 90, 120, 150 and 180 min. Reactions were stopped by pouring the mixtures into a large amount of cold water. The nanocrystals were further ultrasonicated for 15 min in an ultrasonic bath Thornton (USC-1400 model) with frequency of 40 kHz, followed by a prolonged dialysis (regenerated cellulose membrane Fisher, cut-off 10,000–14,000 Da) against pure deionized water to neutral pH. According to Dong [26], this procedure ensured that all ionic materials were removed except the H_3O^+ counterions associated with the sulfate groups on the surface of the nanocrystals. Suspensions of SE-CNC and WSE-CNC were stored in a freezer.

Fig. 1 shows the flowchart of the steps used to obtain SE-CNC and WSE-CNC. At each step the samples were named according to the procedure used.

2.3. Characterization

2.3.1. Acacia bark and cellulose

Structural differences among the samples were revealed using an ATR-FTIR Nicolet 6700 spectrometer through spectra obtained with 64 scans and a resolution of 2 cm^{-1}.

Scanning electron micrographs of samples corresponding to each isolation step were obtained using a JEOL® microscope JSM 6060 operating at 20 kV. The test specimens were attached to an aluminum stub and sputtered with gold.

Wide-angle X-ray scattering experiments were performed using a Siemens D500 diffractometer. SE-cellulose and WSE-cellulose