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A comprehensive approach for obtaining cellulose nanocrystal from coconut fiber. Part I: Proposition of technological pathways

Diego M. do Nascimento[a,*], Jessica S. Almeida[b], Maria do S. Vale[c], Renato C. Leitão[c], Celli R. Muniz[c], Maria Clea B. de Figueirêdo[c], João Paulo S. Morais[d], Morsyleide de F. Rosa[c,*]

[a] Federal University of Ceará (UFC), Department of Chemical, Bloco 940, CEP 60455-760 Fortaleza, Ceará, Brazil
[b] State University of Ceará (UECE), Campus do Itapery, CEP 60455-900 Fortaleza, Ceará, Brazil
[c] Embrapa Tropical Agroindustry, Rua Dra Sara Mesquita 2270, Planalto do Pici, CEP 60511-110 Fortaleza, Ceará, Brazil
[d] Embrapa Cotton, Rua Oswaldo Cruz 1143, Centenário, CEP 58428-095 Campina Grande, Paraíba, Brazil

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ABSTRACT

The high lignin content in the unripe coconut fiber limits the use of this biomass as a cellulose nanocrystal source compared to other cellulose-rich materials. The aim of this study was to obtain lignin and biomethane, and evaluate different approaches for extracting cellulose nanocrystal from unripe coconut coir fiber. The environmental evaluation of these approaches is presented in the second part of this paper. Lignin was extracted by acetosolv pulping and cellulose by alkaline hydrogen peroxide bleaching respectively. Were evaluated the biochemical methane potential of the effluents resulting from acetosolv pulping as well as the lignin concentration. Cellulose nanocrystals were prepared from cellulose pulp via four methods: acidic hydrolysis with high acid concentration, acidic hydrolysis with low acid concentration, ammonium persulfate oxidation, and high-power ultrasound. The cellulose nanocrystals were analyzed by FTIR spectroscopy, X-ray diffraction, transmission electron microscopy, and TG analysis. Using these methods, the whole coconut fiber could be used to produce cellulose nanocrystals and lignin. Among the proposed methods, high-power ultrasound showed the highest efficiency in cellulose nanocrystal extraction.

1. Introduction

Cellulose nanocrystal is an abundant potential nanomaterial that can be extracted from many renewable sources (Dufresne, 2013). This nanostructure has attracted attention for application in several different areas because of its extraordinary physical properties, biodegradability, biocompatibility, and low cytotoxicity (Jorfi and Foster, 2015; Rojo et al., 2015). Cellulose nanocrystals can be obtained from wood, non-wood fibers, algae, tunicates, and agroindustrial biomass, among other sources (Li et al., 2015).

Among the sources, lignocellulosic agroindustrial byproducts are the most promising because of their low cost and availability. Examples include sugarcane bagasse (Li et al., 2012a; Mandal and Chakrabarty, 2014), corn straw (Huntley et al., 2015), palm-pressed mesocarp fiber (Souza et al., 2015), sisal (Rodrigues et al., 2015), pineapple leaves (Deepa et al., 2015), cotton linter (Morais et al., 2013), banana pseudostem (Pereira et al., 2014), banana peel, and unripe coconut husk (Fahma et al., 2011; Nascimento et al., 2014; Rosa et al., 2010). However, the profit ability of new biobased industries highly depends on integrating biomass conversion processes to produce a range of fuels, power, materials and chemicals.

Worldwide coconut production was estimated to be approximately 62 million tons in 2013, of which nearly 3 million tons were harvested in Brazil (FAOStat, 2015). Coconut water is the main product of coconut crops. It is usually consumed directly from the fruit in coastal cities or is bottled for shipping to inland locations. Both processes generate large amounts of unripe coconut coir that if not correctly collected and disposed of, causes environmental problems, reducing the useful lifetime of landfills or causing water pollution.

Unripe coconut fibers can be extracted and used to manufacture several products, such as reinforced polymeric composites, reinforced cement and concrete, geotextile fabrics and screens, and wood-replacement fiberboards. Other alternatives for adding value and reducing the disposal issues of such biomass involve the extraction the cellulose nanocrystals. However, there are

* Corresponding author.
E-mail address: morsyleide@gmail.com (M.d.F. Rosa).

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two main limitations to performing this fractionation: high power and reagent consumption to remove lignin and low yield of cellulose nanocrystals from the original raw material (Figueirêdo et al., 2012). In this sense, all feasible approaches for obtaining cellulose nanocrystals must also add value to other macromolecules, such as lignin and hemicellulose.

Lignin is traditionally considered to be a troublesome waste and is typically burned in mill boilers to generate power (Cotana et al., 2014). Despite this traditional use, lignin has gained attention for industrial applications because of its amorphous nature and highly aromatic molecular structure. Thus, lignin can be used as a raw material for producing bulk and fine chemicals, such as vanillin, gallic acid, oils, phenols, acetic acid, films, polyurethanes, carbon fibers, and other materials (Norgren and Edlund, 2014). Strassberger et al. (2014) report that the low price of natural gas and the diversity of alternatives for lignin conversion is an atractive scenario to use lignin as a chemical instead of a simple fuel to be burned in the boilers. The versatility of fine chemicals that can be produced from lignin makes this biomacromolecule as lower carbon footprint alternative to oil, reducing environmental impacts related to climate change (McDevitt and Grigsby, 2014). In addition to lignin and cellulose, the coconut fiber contains high hemicellulose levels that typically are hydrolyzed during the extraction processes. Such compounds are present in the effluents of cellulose pulp and can be used as carbon sources for anaerobic fermentation and methane production. Methane has a calorific power (~50 MJ/kg) higher than lignin (~21 MJ/kg) and hemicelluloses (~16 MJ/kg). The gas can be burned to generate power for the nanocrystal extraction process, reducing biogas production and emission in the effluents.

The aim of the present study was to develop new approach for unripe coconut, allowing for the sustainable extraction of cellulose nanocrystal and to add value to the extraction byproducts. Lignin was recovered and pulping effluents were fermented to produce methane. Here, the properties of the extracted cellulose nanocrystal are reported. In the Part II, the environmental impacts of the extraction methods are evaluated with respect to life cycle analysis.

2. Experimental

2.1. Materials

Unripe coconut fiber was provided by Embrapa Agroindústria Tropical (Fortaleza, CE, Brazil). All chemicals were of analytical grade and were used without further purification: 97% (w/w) NaOH, 30% (w/w) H_2O_2, 99.7% (w/w) CH_3COOH, 80% (w/w) $NaClO_2$, and 98% (w/w) H_2SO_4 (Vetec Química Fina Ltda/Sigma–Aldrich—Duque de Caxias, RJ, Brazil).

2.2. Coconut fiber fractioning

The fractionation flowchart is presented in Fig. 1. Coconut fiber was ground in a Willye knife mill (STAR FT-80; Fortinox, Piracicaba/SP, Brazil) with a 1-mm-large sieve. Delignification was performed as described by Nascimento et al. (2014) with slight modifications.

Briefly, after grinding, the fiber was added to acetosolv solution containing 93% (w/w) acetic acid and 0.3% (w/w) HCl in the ratio of 1:20 (w/v), heated under continuous reflux and stirring for 3 h. After pulping, the fibrous material was filtered through a Whatman no 2 paper filter and rinsed with fresh acetosolv solution at 80 °C. The black liquor, this effluent from this step, was stored for later lignin recovery. The delignified cellulose pulp was rinsed with water until the pH was neutral.

The fiber was bleached in the proportion of 1:20 (w/v). First, the pulp was stirred for 90 min at 50 °C with 5% (w/w) H_2O_2 and 3.8 (w/w) NaOH. The bleached pulp was filtered through a Whatman no 2 paper filter and rinsed with distilled water. This bleaching process was repeated once more. Finally, the fibers were stirred with 5.7% (w/w) KOH for 120 min at 90 °C, filtered through a Whatman no 2 paper filter, and rinsed with distilled water to obtain the cellulose bleached pulp (Fahma et al., 2011).

The pulping black liquor was concentrated in a rotary evaporator (R-210/215; Buchi, Flawil, Switzerland), diluted 10× in hot water (~80 °C), filtered through Whatman no 2 paper filter, and rinsed with distilled water to recover lignin. The recovered lignin was stored in a silica-gel desiccator until characterization analyses (Morandium-Gianetti et al., 2012). The yield of recovered lignin, the percentage of Klason lignin in the fiber that was successfully recovered, was calculated using Eq. (1):

$$\%Y_{\text{recovered lignin}} = \frac{m_{\text{recovered lignin}}}{m_{\text{fiber}} \times \%LK_{\text{fiber}}} \times 100 \quad (1)$$

where $m_{\text{recovered lignin}}$ is the weight of the recovered lignin, m_{fiber} is the weight of the coconut fiber and$\%LK_{\text{fiber}}$ is the lignin Klason contents of the samples.

The pulping effluent of the lignin recovery (effluent A) (172 mL of effluent/1 g of coconut fiber) and the mixed effluent of bleaching and lignin recovery (effluent AB) were collected (397 mL of effluent/1 g of coconut fiber) and analyzed to determine the biodegradability and biochemical methane potential (BMP) assays via anaerobic digestion.

2.3. Cellulose nanocrystal extraction

Cellulose nanocrystal extraction was performed using four different methods: two acidic hydrolysis-based extractions, one

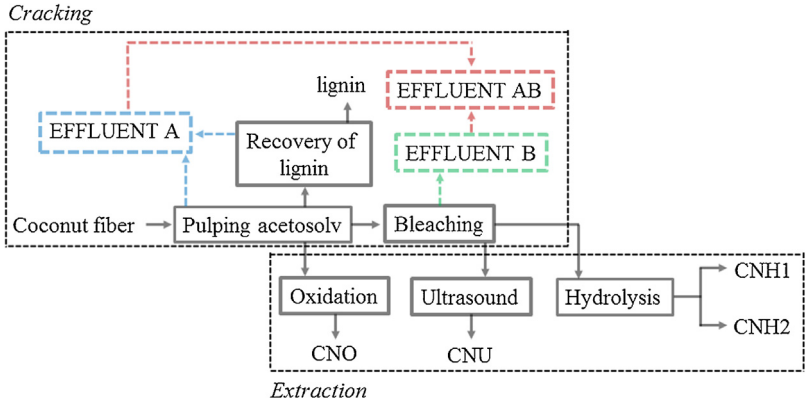

Fig. 1. General flowchart of coconut fiber fractionation.