



Isolation and characterization of cellulose nanofibrils from arecanut husk fibre



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ABSTRACT

The isolation of cellulose nanofibres from arecanut husk was achieved by a chemo-mechanical method thereby opening up a means for utilizing a waste product more effectively. The chemical processes involved alkali treatment, acid hydrolysis, and bleaching. The mechanical fibrillation was performed via grinding and homogenization. The chemical constituents at different stages of treatment of fibres were analyzed according to the ASTM standards. Morphological characterization was done using the scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The isolated nanofibers had an average diameter of below 10 nanometres and a very high aspect ratio in the range 120–150. Fourier transform infrared spectroscopy (FT-IR) showed the effective removal of the non cellulosic components. The crystallinity was increased with successive treatments as shown by the X-ray diffraction analysis (XRD). The TGA studies revealed a good thermal stability for the isolated nanofibres.

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1. Introduction

With the development of nanotechnology, cellulose, one of the most ancient and abundant natural polymer on earth, attracts more attention in a new form: 'nanocellulose'. Based on the dimension and morphology, nanocellulose is grouped as cellulose nanocrystals (CNC), cellulose nanofibers, (nanofibrillated cellulose) and bacterial cellulose or microbial cellulose (Dufresne, 2012; Klemm et al., 2011). Among these cellulose nanofibers have gained much attention from academic and industrial researchers, especially for the development of new bio nanocomposite materials (Charreau et al., 2013; Khalil et al., 2014; Missoum, Belgacem, & Bras, 2013; Song, Winter, Bujanovic, & Amidon, 2014). Cellulose nanofibre composites find applications in many areas such as printed and flexible electronics films and coatings for packaging, drug delivery, water treatment, optical media, barrier films, etc. The use of nanocellulose based composites in automotive and building products is increasing. Over the years, numerous studies have been carried out for the extraction of cellulose nanofibres from various cellulosic sources, such as oil palm biomass (Fahma, Iwamoto, Hori, Iwata,

& Takemura, 2010; Fahma, Iwamoto, Hori, Iwata, & Takemura, 2011; Khalil et al., 2014; Nazir, Wahjoedi, Yussof, & Abdullah, 2013) wood pulp (Siddiqui, Mills, Gardner, & Bousfield, 2011), kenaf, (Chan, Chia, Zakaria, Ahmad, & Dufresne, 2012; Jonoobi, Khazaeian, Tahir, Azry, & Oksman, 2011), bamboo (Yu et al., 2012), flax (Khalil, Mahayuni, Rudi, Almulali, & Abdullah, 2012; Qua, Hornsby, Sharma, & Lyons, 2011) and rice straw (Lu & Hsieh, 2012). Utilization of these lignocellulosic fibres increase rapidly due to their abundance and ease of recyclability and attractive properties.

Several methods have been reported for the extraction of nanocellulose fibres from these renewable sources. A chemo-mechanical method was used by Alemdar et al. for the extraction of cellulose nanofibres from the agricultural residues such as wheat straw and soy hulls for use as reinforcement in biocomposites. (Alemdar & Sain, 2008). They obtained cellulose nanofibres with 10–80 nm diameter and 35% improvement in crystallinity for wheat straw nanofibres and only 16% for soyhull nanofibres. Farah Fahma and co-workers extracted cellulose nanofibres by hydrolysing oil palm empty fruit bunch with sulphuric acid hydrolysis (Fahma et al., 2010). They observed a decrease of crystallinity and DP with sulphuric acid treatment time. Fatah et al. explored a chemo-mechanical technique to isolate cellulose nanofibres from oil palm empty fruit bunch (OPEFB) and succeeded in

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obtaining cellulose nanofibres of diameter in the range 5–10 nm and found a reduction in crystallinity which is influenced by the pressure of mechanical treatment (Fatah et al., 2014). Chemical ultrasonic method was adopted by Chen et al. for isolating cellulose nanofibres from four different fibres, wood, bamboo, wheat straw and flax fibres. They succeeded in isolating nanofibres with diameter ranging from 10 to 40 nm from wood, bamboo and wheat straw whereas flax fibres with high cellulose content were not uniformly nanofibrillated (Chen et al., 2011). Saito et al. introduced an oxidation pre treatment of cellulose with 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated system. They obtained cellulose nanofibres with 3–4 nm width from hardwood celluloses (Saito et al., 2009). The defibrillation of nanofibrillated cellulose usually require intensive mechanical methods such as microfluidization, cryocrushing, grinding, high intensity ultrasonication, high pressure homogenization or a combination of these (Khalil et al., 2014). Kanoth et al. obtained highly crystalline nanofibrillated cellulose of diameter 18–20 nm from coir by using a commercial kitchen grinder for pulping followed by chemical treatment. An Ultra Turrax homogenizer was used for nanofibrillation of the chemically pretreated and bleached pulp (Kanoth, Thomas, Joseph, Kuthirummal, & Narayanankutty, 2015).

Among all lignocellulosic fibres, areca appears to be a promising material because of its abundance being a perennial crop and less cost. Areca belongs to the species *Areca catechu* under Arecaceae family and believed to have originated in either Malaysia or Philippines. It is found in much of the tropical Pacific, Asia and parts of East Africa. Areca nut is used for chewing in some Asian countries. In India, areca cultivation is increasing in a large scale to attain self sufficiency in paint, medicine, chewable gudka, etc. Arecanut husk constitutes about 60–80% of its total weight and volume of the fresh fruit. Arecanut husk is a waste product and is mostly used as a fuel for areca nut processing. Areca husk left unnoticed in the plantation causes bad odour and other decay related issues. A few articles have been reported to utilize the arecanut husk fibre as a reinforcing material in epoxy, UF and PF composites (Srinivasa & Bharath, 2011; Srinivasa et al., 2011). The utilization of this lignocellulosic fibre in polymeric composites will open up a new way of disposing off a waste product. A better understanding of chemical composition, morphology, physical and thermal properties of the nanofibres after isolation from arecanut husk fibre will be useful in developing new bionanocomposites.

Arecanut husk consists mainly of cellulose, hemicelluloses, and lignin. The cellulose contains much more crystalline regions whereas hemicelluloses and lignin are amorphous in nature. The noncellulosic constituents of fibres are removed during the extraction process. The amorphous regions easily absorb chemicals and undergo hydrolysis while the compactness of crystalline regions resists the penetration of chemicals (Klemm et al., 2006). Alkaline treatment is usually done to remove the hemicelluloses and lignin. It is well known that when acid hydrolysis is used the properties, the structure and the size of the nanocellulose depend on the raw material, concentration and the time of hydrolysis (Habibi, Lucia, & Rojas, 2010). This study aims at isolating cellulose nanofibres from a renewable, inexpensive and underutilized raw material-arecanut. To date, no study has been reported on the isolation of cellulose nanofibres from arecanut husk. Controlled hydrolysis using hydrochloric acid coupled with mechanical pre treatment (using a simple kitchen grinder) followed by homogenization (using ultra Turrax homogenizer) was adopted for the isolation of cellulose nanofibres (Kanoth et al., 2015). The resultant nanofibres were characterized by various techniques. The morphology and physico-chemical properties were analyzed by SEM, FE-SEM, TEM, XRD, DLS, FTIR and TGA.

2. Experimental

2.1. Materials and methods

Dried arecanut husk was collected from the western coastal region of Kerala, South India. The fibres were separated from the husk by the biological retting process. Toluene, ethanol, sodium hydroxide, con hydrochloric acid, sodium chlorite, acetic acid and all other chemicals used for the extraction process were of analytical grade.

2.2. Isolation of cellulose nanofibrils

Fig. 1 shows the overall process flow chart. The dried areca husk fibres were dewaxed with a (2:1, v/v) mixture of toluene and ethanol for 48 h at 50 °C followed by washing with boiling water and dried in air. The dried fibres were then cut into short fibres of 6 mm length. The major part of the lignin and hemicelluloses was removed by treating with 5% NaOH solution at a temperature of 50 °C for 4 h. It was then washed free of alkali and treated with 3.5 M con HCl to break up the cell walls and thus to separate microfibrils (Boldizar, Klason, Kubat, Näslund, & Saha, 1987). The fibres were washed well with deionised water to get rid of acid. Then it was grinded into a pulp form and treated again with alkali to remove the remaining noncellulosic constituents followed by acid hydrolysis with 5 M acid (Bipinbal, 2012; Kanoth et al., 2015).

The delignification was further carried out by the bleaching process proposed by Wise, Murphy, & D'Addieco (1946). The delignified fibres with a solvent to fibre ratio of 25:1 by weight were bleached with a 4:1 mixture of sodium chlorite (NaClO₂) and glacial acetic acid for 2 h at 60 °C. The bleaching was repeated with half the initial amount of bleaching agent. After bleaching, the fibres were washed with deionised water until the pH 7. The white suspension obtained was then homogenized in an Ultra Turrax homogenizer (IKA Homogenizer model T25 digital S22) at 12,000 rpm for 2 h to get nanofibrillated cellulose.

3. Characterization

3.1. Analysis of chemical composition

Chemical constituents of the raw fibre and at each stage of treatment were measured according to ASTM standards. α -cellulose (ASTM D 1103-55T), hemicelluloses (ASTM D 1104-56), lignin (ASTM D1106-56), moisture content (ASTM D 4442-92) of raw and treated fibre along with the pectin content and ash content of the raw fibre were determined.

3.2. Fourier transform infra red spectroscopy (FT-IR)

FT-IR spectra were recorded on a Fourier transform infrared (FT-IR) instrument (Thermo Nicolet, Avatar 370) in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. FT-IR spectra of the raw fibre, alkali treated, acid hydrolysed after grinding and bleached pulp were taken by attenuated total reflection (ATR) technique. The peak heights were determined from the absorbance spectra using EZ OMNIC software.

3.3. Scanning electron microscopy (SEM)

The morphological analysis of raw fibre and treated fibres was done using a JEOL Model JSM.6390 LV scanning electron microscope. The fibre surfaces were gold coated prior to SEM investigation to make them conductive.

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