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Isolation and characterization of cellulose nanofibers from culinary banana peel using high-intensity ultrasonication combined with chemical treatment

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In the present study, culinary banana peel was explored as a source of raw material for production of cellulose nanofibers (CNFs). For isolation of CNFs, first the peel flour was subjected to different chemical treatments to eliminate non-cellulosic compounds. The obtained chemically treated cellulose fibers were then mechanically tailored and separated into nanofibers using high-intensity ultrasonication at different output power ranging from 0 to 1000 W. The presences of nanofibers in all samples were confirmed by TEM. Increasing output power of ultrasonication reduced size of CNFs and generated more thinner and needle-like structure. SEM, FT-IR and XRD results indicated chemical treatment employed was effective in removing compounds other than cellulose fibers. Thermal analyses evinced the developed CNFs enhanced thermal properties which serve the purpose as an effective reinforcing material to be used as bionanocomposites. Hence, the production of CNFs from this underutilized agro-waste has potential application in commercial field that can add high value to culinary banana.

1. Introduction

Cellulose the homopolysaccharide representing about 1.5×10^{12} tons of total annual biomass production composed of glucose–glucose linkages (β-1,4-linked-glucopyranose unit) arranged in linear chains where C-1 of every glucose unit is bonded to C-4 of the next glucose molecule and nanostructures (Kadla & Gilbert, 2000; Kim & Yun, 2006; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011;). It is one of the most important biopolymers in existence and is derived from readily available biomass (Abraham et al., 2011). Due to its availability, biocompatibility, biodegradability and sustainability cellulose is widely used (Chen et al., 2011). Cellulose fibers exhibit a unique structure hierarchy derived from their biological origin. They are composed of assemblies of nanofiber diameter ranging 2–20 nm and a length of more than a few micrometers. The nanometer-sized single fiber of cellulose is commonly referred to as nanocrystals, whiskers, nanowhiskers, microfibrillated cellulose, microfibril aggregates or nanofibers (Chen et al., 2011; Eichhorn et al., 2010; Siro & Plackett, 2010). Plants and woods are the primary source of cellulose nanofibers and their compounds encompass current area of research and compared with the commercially available fibers, nanofibers obtained from plant sources poses low density, nonabrasive, combustible, nontoxic, low cost, biodegradable and has good thermal and mechanical properties (Eichhorn et al., 2010; Kalia et al., 2011; Siqueira & Dufresne, 2009).

The study of cellulose nanofibers as a reinforcing phase in nanocomposites started almost 15 years ago. Since then, cellulose nanofibers unlock the door in the direction of promising research on cellulose-based nano materials with increasing area of potential applications including packaging material (Rodionova et al., 2011; Spence, Venditti, Rojas, Pawlak, & Hubbe, 2011), transparent material (Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009; Iwamoto, Abe, & Yano, 2008), paper production (Henriksson, Berglund, Isaksson, Lindstrom, & Nishino, 2008; Yoo & Hsieh, 2010) biomedical application (Cherian et al., 2011; Czaja, Young, Kawecki, & Brown 2007). Cellulose nanofibers could also be used as a rheological modifier in foods, paints, cosmetics and pharmaceutical products (Turbak, Snyder, & Sandberg, 1983). Many studies have been done on isolation and characterization of cellulose nanofibers from various sources such as wood fibers (Abe, Iwamoto, & Yano, 2007), cotton (de Morais et al., 2010), potato tuber cells (Dufresne, Dupeyre, & Vignon, 2000), prickly pear fruits (Habibi, Heux, Mahrouz, & Vignon, 2008), lemon and maize (Rondeau-Mouro et al., 2003), soybean (Wang & Sain, 2007), wheat straw and soy hulls (Alemdar & Sain, 2008a), coconut husk fibers

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(Rosa et al., 2010), branch-barks of mulberry (Li et al., 2009), pineapple leaf fibers (Cherian et al., 2010), banana rachis (Zuluaga et al., 2009), pea hull fiber (Chen, Liu, Chang, Cao, & Anderson, 2009) and sugar beet (Dinand, Chanzy, & Vignon, 1999). There has been growing interest in researching the potentiality of using cellulose-based nanofibers as a reinforcing material. Cellulose nanofibers can be extracted from the cell walls by chemical and/or mechanical treatment such as cryocrushing (Chakraborty, Sain, & Kortschot, 2006), grinding (Abe & Yano, 2010; Abe, Nakatsubo, & Yano, 2009; Abe et al., 2007), high-pressure homogenization (Pelissari, Sobral, & Menegalli, 2014), acid hydrolysis (Elazzouzi-Hafraoui et al., 2008; Liu, Liu, Yao, & Wu, 2010) and biological treatment, like enzyme-assisted hydrolysis (Paakko et al., 2007; Tibolla, Pelissari, & Menegalli 2014).

Use of ultrasonic technique for isolation of cellulose nanofibers is an emerging method and has been extensively used by various researchers (Cheng, Wang, & Rials, 2009; Cheng, Wang, & Han, 2010; Chen et al., 2011; Wang & Cheng, 2009). During the process of ultrasonic treatment, ultrasound energy is transferred to cellulose chains through a process called cavitation, which refers to the formation, growth and violent collapse of cavities in water (Chen et al., 2011). The energy provided by cavitation in this so-called sonochemistry is approximately 10–100 kJ/mol, which is within the hydrogen bond energy scale (Tischer, Sierakowski, Westfahl, & Tischer, 2010). Thus, the ultrasonic impact can gradually disintegrate the micron-sized cellulose fibers into nanofibers.

In the process of development of value-added food products from culinary banana, the peel is a waste material of various fruit and vegetables processing units located in Northeast India. Therefore, it is possible to obtain banana peel sufficiently and application depends on its chemical compositions (Emaga, Andrianaivo, Wathelet, Tchnago, & Paquot, 2007). Literature revealed hitherto unexploited of this biomaterial in terms of its value addition and has enormous potential for its industrial use. Hence, the use of this biomaterial will not only help in increasing value addition but also help the environment from pollution free. The only culinary variety of banana found in entire region of Assam and in North Eastern state of India is *Musa* ABB which is locally called as *kachkal* is an important and cheap source of vegetable in the livelihood of regional people (Khawas, Das, Sit, Badwaik, & Deka, 2014a; Khawas, Das, Dash, & Deka, 2014b; Khawas, Dash, Das & Deka, 2015). Knowing the fact that, peel of culinary banana (*kachkal*) is an abundant source of cellulose, it can be considered as a potential candidate for development of reinforcing composites. As mentioned earlier many researchers have reported their work on cellulose nanofibers from different sources; however, there is hardly any work reported on cellulose nanofibers from culinary banana peel. In the light of the above-stated reasons, the aim of this present study was to add value to culinary banana peel by isolating its cellulose nanofibers using chemical treatment followed by high-intensity ultrasonication. The developed material can be used as a reinforcement material in high-performance biocomposites and also it will help the environment to be waste free.

2. Materials and methods

2.1. Raw materials and chemicals

Fresh culinary bananas (*kachkal*) variety *Musa* ABB at mature edible stage was collected from local agricultural farm in Tezpur, Assam (India). The samples were cleaned thoroughly with running tap water followed by soaking in double-distilled water for 1 h to remove any dust or dirt adhering to the peel surface and finally wiped with tissue papers and peel flour was prepared. All chemicals used in the present study viz. acetic acid (CH_3COOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium metabisulphite ($K_2S_2O_5$), sodium chlorite ($NaClO_2$), anthraquinone ($C_{14}H_8O_2$), sulfuric acid (H_2SO_4) were analytical reagent grade and procured form HiMedia Laboratories, India.

2.2. Preparation of peel flour

Previously cleaned culinary bananas were peeled manually and pulp was separated from peel. The peels were then immediately dipped in solution of 1% potassium metabisulphite for 12 h to inhibit oxidation and enzymatic browning. Subsequently, the peels were dried at 50 °C for 24 h by using convective tray dryer (Model No. IK-112, Make IKON Instruments, Delhi). The dried peels were ground and passed through 0.25 mm mesh screen, packed in polyethylene bags and stored at 4 °C.

2.3. Isolation of cellulose fibers (CFs) and cellulose nanofibers (CNFs)

The culinary banana peel flour (yield was 63.35%) having moisture content (6.7%), cellulose (16.62%), hemicelluloses (7.34%), lignin (4.01%) was given first alkali treatment by cooking in a digester (KelPlus, Pelican Equipment, India) with a solution of 20% (w/v) sodium hydroxide and 0.1% anthraquinone with peel flour to solution ratio (1:20) at 170 °C for 1.5 h which partially solubilized pectin, lignin and hemicelluloses. The digested peel was washed with distilled water to remove those pectin, lignin and hemicelluloses. The insoluble pellets remained after the first alkali treatment was further delignified with 1% (w/v) sodium chlorite (at pH 5 adjusted with 10% (v/v) acetic acid) at 70 °C for 1 h. The insoluble pellets remained after first bleaching treatment was washed and second bleaching treatment was given again, maintaining the same condition as in the first bleaching process which resulted in further effective discoloration and confirming the leaching out of phenolic compounds and lignins. The neutralized insoluble pellets remained after second bleaching process were subjected to second alkali treatment with 5% (w/v) KOH solution at ambient temperature (25±2 °C) for 15 h followed by washing which helped in elimination of residual hemicelluloses. Finally, the insoluble pellets were given to acid hydrolysis treatment with solution of 1% (v/v) sulfuric acid at 80 °C for 1 h. The acid hydrolysis treatment helped in leaching out traces of minerals, residual starch and also hydrolyzed amorphous cellulose and eased in getting the required nanofibers. After each step of chemical treatment, the insoluble pellets were washed with double-distilled water and centrifuged at 10,000 rpm at 4 °C for 20 min until the pellets were neutralized. The pellets were kept in water-swollen state during whole chemical process in order to avoid generating strong hydrogen bonding among nanofibers.

The chemically purified cellulose fibers were soaked in deionized water (concentration ~0.5% mass) and subjected to tailoring and size reduction by giving high-intensity ultrasonic treatment. The solution of chemically purified cellulose fibers (120 ml) was placed in ultrasonic generator (UW 2070, Bandelin sonoplus, Germany) having 1.5 cm (diameter) cylindrical titanium alloy probe tip at frequency of 25 kHz. Ultrasonication was carried out for 30 min in order to isolate the cellulose nanofibers. The output power of ultrasonication was conducted at 400, 800 and 1000 W individually to characterize the effect of ultrasonic intensity on nanofibrillation of chemically purified cellulose. The ultrasonic treatment was carried out in ice water bath and ice was maintained throughout the sonication time. The detailed steps followed to obtain cellulose nanofibers are illustrated in Fig. 1. The obtained nanofibers were freeze dried (LDF 5512, Daihan Labtech Co., South Korea) and stored at 4 °C in sealed containers.