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Isolation and characterization of cellulose nanofibers from the aquatic weed water hyacinth—*Eichhornia crassipes*

Marimuthu Thiripura Sundari, Atmakuru Ramesh*

Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT), Padappai 601301, Kancheepuram District, Tamil Nadu, India

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ABSTRACT

The cellulose nanofibers from the water blocking aquatic weed—water hyacinth was successfully prepared. The crude and pure cellulose microfibers were initially obtained from the weed plant by following chemical treatments such as bleaching, alkaline and sodium chlorite reactions. The micron-sized fibers obtained from the stems were cryocrushed with liquid nitrogen to release the bundles of nanofibers and followed the sonication for individualization of fibers. The treated fibers were screened through Fourier Transform Infrared Spectroscopy (FTIR) to confirm the removal of impurities from the fibers. The surface morphology of the aqueous suspension before cryocrushing and after the sonication process was investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermal stability of the fiber was increased after chemical treatment; this was confirmed by thermogravimetric analysis (TGA). The synthesized nanofibers were in the diameter range of 20–100 nm from the SEM and 25 nm from the TEM analysis.

1. Introduction

Nanofibers obtained from fiber based natural sources have major potential applications in preparation of reinforced composites, biodegradable thin films, adsorbents, filters, etc., Nanofibers are synthesized from these natural plant based fiber resources following the any one of the method or in combination of the methods chemical and mechanical treatment, enzymatic treatment, oxidative reaction and electrospinning.

Cellulose nanofibers were reported from sources like hemp fiber (Wang, Sain, & Oksman, 2007), soyabean (Wang & Sain, 2007), sugar beet Pulp (Leitner, Hinterstoisser, Wastyn, Keckes, & Gindl, 2007), wheat straw and soy hulls (Alemdar & Sain, 2008), sugarcane bagasse (Bhattacharya, Germinario, & Winter, 2008), sisal (Moran, Alvarez, Cyras, & Vazquez, 2008), banana rachis (Zuluaga et al., 2009), cassava bagasse (Teixera et al., 2009), wood flour (Nogi, Iwamoto, Nakagaito, & Yano, 2009), raw kenaf fibers (Jonoobi, Harun, Mathew, Hussein, & Oksman, 2010), flax fibers (Qua, Hornsby, Sharma, Lyons, & McCall, 2009), softwood, rice straw and potato tuber (Abe & Yano, 2009), cotton (Teixeira et al., 2010), oil palm empty fruit bunch (Fahma, Iwamoto, Hori, Iwata, & Takemura, 2010), refined, bleached beech pulp (Eyholzer et al., 2010). The combination of enzymatic treatment and mechanical shearing resulted in preparation of microfibrillated cellulose (MFC) nanofibers from commercial bleached wood sulphite pulps (Henriksson, Henriksson, Berglund, & Lindstrom, 2007). Electrospinning set up is the latest and the easiest technology for the nanofiber production; it can be used to directly spun from the polymer solutions (Kulpinski, 2005; Ohkawa, Hayashi, Nishida, Yamamoto, & Ducreux, 2009). The TEMPO (2, 2, 6, 6-tetramethylpiperidine-1-oxy radical) mediated catalytic oxidation method was used to produce nanofibers from native celluloses in aqueous conditions under alkaline pH. This is the selective oxidization process of converting C6 primary hydroxyl groups of fiber into carboxylate groups via aldehyde mechanism under appropriate conditions (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006). A viscous and transparent gel was obtained by agitating the oxidized cellulose fiber in blender type homogenizer or ultrasonic homogenizer (Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009; Saito et al., 2006b). The gel has individual nanofibers of 4–6 nm (Okita, Saito, & Isogai, 2009) in width. The water insoluble fractions of oxidized celluloses were used for the determination of carboxyl and aldehyde content (Praskalo et al., 2009) and transparent films were prepared by filtration of TEMPO oxidized cellulose nanofiber through Polytetrafluoroethylene (PTFE) membrane (Fukuzumi et al., 2009).

The literature indicate the extensive preparation of nanofibers from various sources of plants, fruits, vegetables, etc., however, there are no data indicating the utilization of deadly aquatic weeds. The abundant aquatic weed species, *Eichhornia crassipes* (Water hyacinth) in tropical weather conditions is a major problem in open water bodies like power generation, irrigation and boating. Huge amounts are being spent worldwide to selectively remove the weed. The weed is rich in fiber content and has no major differences

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* Corresponding author. Tel.: +91 44 27174246/66; fax: +91 44 27174455.
E-mail address: raamesh_a@yahoo.co.in (A. Ramesh).

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in the percentage of cellulose content in the shoot and root (Zhou et al., 2009). In this study, *E. Crassipes* was used as a fiber sources for the synthesis of cellulose nanofibers. The cellulose nanofibers are isolated using the chemical and mechanical treatment. The characterization of these nanofibers was done by SEM, TEM, FTIR and TGA. The synthesized nanofibers from the above method have the diameter range of 20–100 nm and in several micrometers length. The isolated nanofibers have future use for the preparation of bio-nanocomposites films.

2. Experimental

2.1. Materials and methods

The aquatic weed plant water hyacinth was used as a primary source in the study. The plant stems were collected from the local ponds of Chidambaram, Tamil Nadu, India. The stems were washed with water, dried, chopped and stored at room temperature. The chemicals Toluene, ethanol, sodium hydroxide, sodium chlorite, acetic acid, potassium bromide, liquid nitrogen used in the study are analytical grade reagents.

2.2. Isolation of water hyacinth nanofibers (WHN)

2.2.1. Chemical treatment

2.2.1.1. Synthesis of water hyacinth fibers. The chopped water hyacinth weeds were dewaxed in a soxhlet apparatus with 2:1 (v/v) mixture of toluene/ethanol for 6 h. The dewaxed fibers were bleached and boiled with 3 wt.% sodium chlorite solutions under acidic condition at pH 4. The suspension was maintained for 3 h at 80 °C and allowed to settle over night. The process was repeated twice, washed with distilled water until free from acid and the white tissues were achieved. The hemicellulose was removed from the obtained tissue by treating with 1 wt.% of sodium hydroxide solution at 60 °C for 24 h. The samples were centrifuged and washed with distilled water. The lignin was removed by further treatment with 1 wt.% sodium chlorite solution under acidic condition and stirred well at 75 °C for 48 h; the samples were centrifuged and washed with distilled water. The remaining hemicelluloses was removed and resulted to pure cellulose fibers by treating with 5% of NaOH solution at 55 °C for 24 h with continuous stirring. Finally centrifuged the obtained residues and washed with distilled water till free from alkali.

2.2.2. Mechanical treatment

The chemically treated samples were further broken down into fragments by the mechanical treatment using high shear, high-energy transfer and high impact. (Bhatnagar & Sain, 2005).

2.2.2.1. Ball milling. The purified cellulose fibers obtained from the chemical process, was dried at 100 °C for 24 h, followed by micronisation of water hyacinth fibers using a centrifugal ball mill (Retsch PM100, Germany). In a 50 ml cap, 5 g of sample with 10 pieces of 10 mm of Agate balls were used and centrifuged for 20 min at 550 rpm/min.

2.2.2.2. Cryocrushing and sonication of chemically treated fibers. The ball milled fibers were dispersed in water and then nanofibers were released by cryocrushing in a mortar with a pestle by applying high impact then ultrasonicated for 15 min to obtain the uniform dispersion of nanofibers in water. The sonicated suspensions were lyophilized to obtain the cellulose nanofiber.

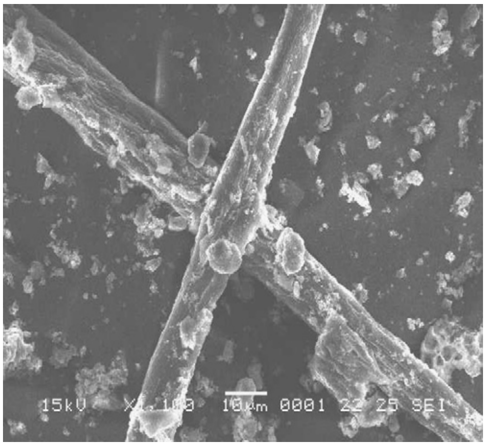

Fig. 1. SEM image of bleached raw water hyacinth fibers.

2.3. Characterizations

2.3.1. Optical microscopy

The fiber morphology was observed using the optical microscopy (Zeiss, Germany).

2.3.2. Scanning electron microscopy (SEM)

The morphology of the cellulose fibers and nanofibers were investigated using shimadzu scanning electron microscopy. The samples before cryocrushing and after the sonication process were mounted in aluminum stub,coated with platinum/gold by an ion

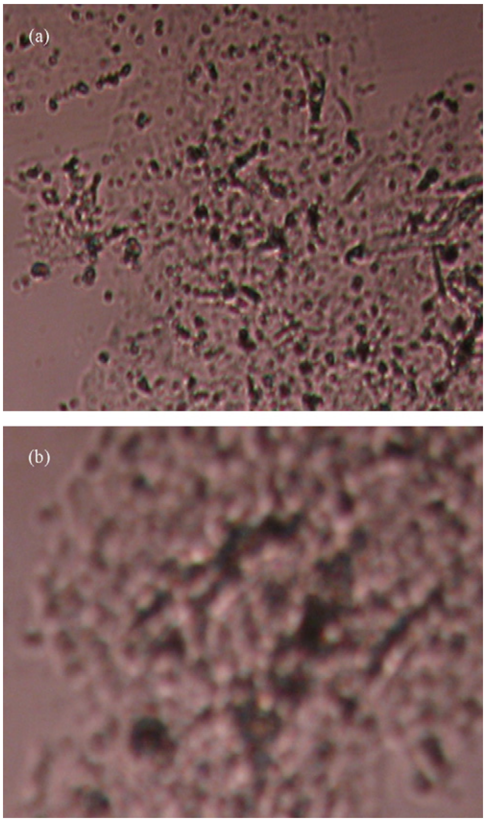

Fig. 2. Obtain the purified cellulose fibers from the successive chemical treatment of crude fibers evidenced by an optical micrographic image (a) at 10× and (b) at 100× magnifications.

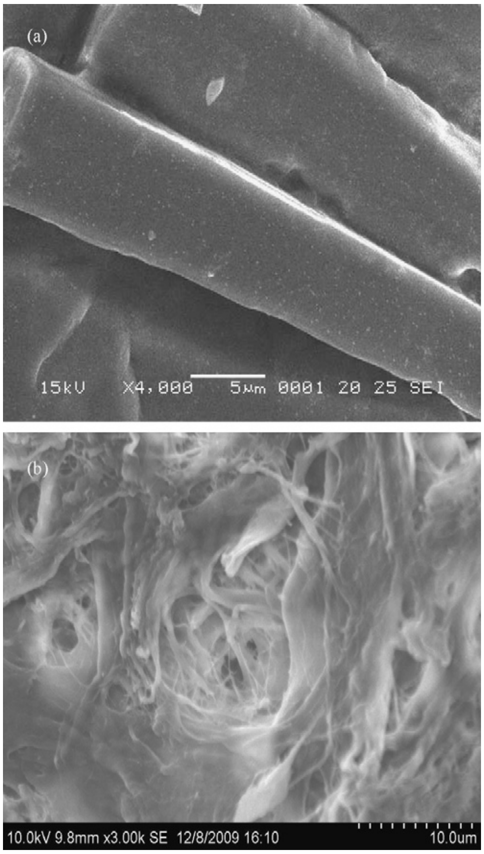

Fig. 3. SEM images (a) at 4K and (b) at 3K magnifications.

sputter coater to prevent charging and scanned using SEM. From the SEM images, the diameters were calculated using the image tool analyzer.

2.3.3. *Transmission electron microscopy (TEM)*

A drop of diluted nanofiber suspension was mounted in a carbon coated grid and placed in transmission electron microscopy (TEM), operating at 20–200 kV with a resolution of 2.4 Å and the TEM images were captured and the fiber diameters were calculated using the image tool analyzer.

2.3.4. *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR spectroscopy was used to examine the changes in the chemical composition of the chemically treated fibers obtained from water hyacinth. The dried samples of the original crude and treated fibers were crushed into powder and a thin pellet was made by mixing with potassium bromide (KBr) and scanned in Shimadzu Fourier Transform Infrared Spectroscopy (FTIR 8400S) to obtain the FTIR spectra. The spectrum was obtained in the transmission mode and the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} with 40 scans per each sample.

2.3.5. *Thermogravimetric analysis (TGA)*

The thermal characteristics of the original crude and treated cellulose fibers was studied using a Thermogravimetric analyzer (TGA), at a temperature range 50–700 °C in a nitrogen atmosphere at a heating rate of 20 °C/min.

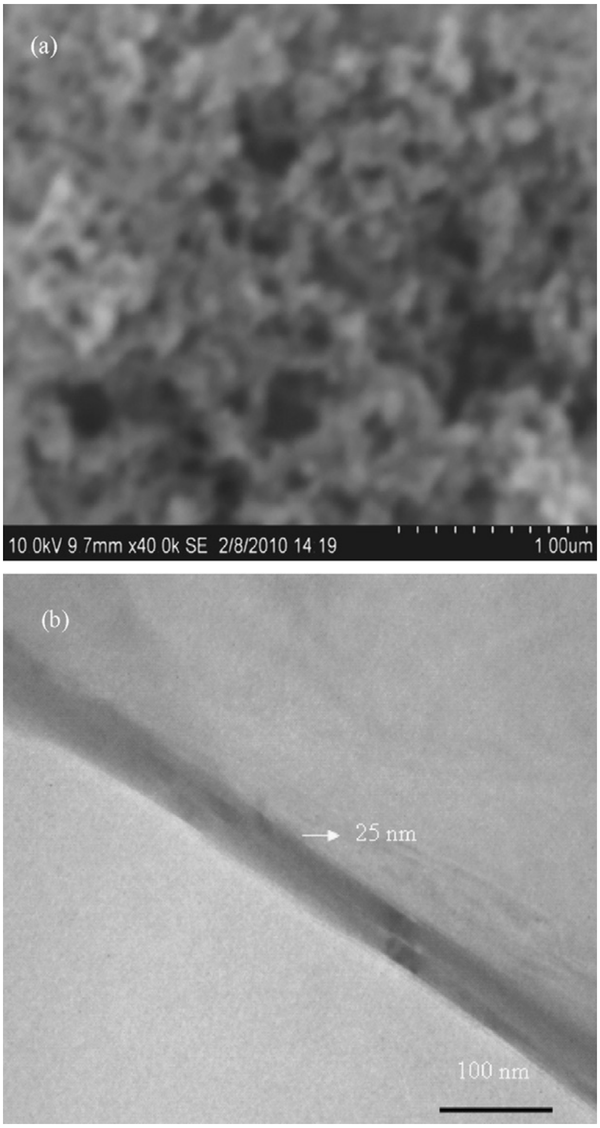

Fig. 4. (a) SEM image of bundles of cellulose nanofibers before sonication showing <100 nm; (b) TEM image showing a single cellulose nanofiber after sonication with a diameter of 25 nm.

3. Results and discussion

3.1. *Morphology of the water hyacinth fibers at various treatments*

The cellulose fibers were obtained by successive treatments of raw water hyacinth fibers for the removal of hemicelluloses, lignin, pectin and other soluble components using acidified sodium chlorite and sodium hydroxide solutions. A bleached water hyacinth fiber is in the size 25–50 μm (Fig. 1). Optical micrographs (at different magnifications Fig. 2a and b) reveal that the chemical treatment resulted in the bundles of fibers and the hemicelluloses, lignin and the other solubilised impurities were removed.

The SEM image after the chemical treatment (Fig. 3a) at 4 K magnification represents the individual cellulose fibers at a diameter of 7 μm and (Fig. 3b) at 3 K magnifications shows the clusters of fibers with a diameter range of one to two micrometers and lengths in several microns. During the mechanical treatment, cellulose fibers were ball milled in which the fibers were reduced in size up to submicron level, followed by cryocrushing process has resulted the agglomeration of fibers and moderately reduced the

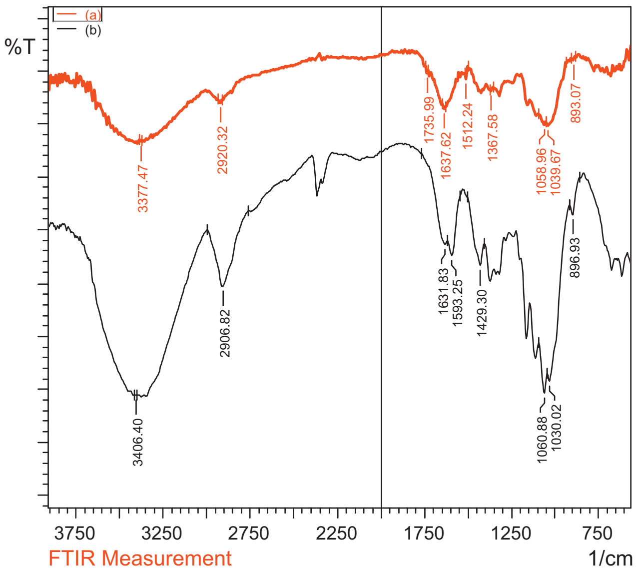

Fig. 5. FTIR spectra of (a) original crude fibers and (b) cellulose nanofibers of water hyacinth.

fiber sizes. The cryocrushed fibers were sonicated for 15 min to obtain the uniformly dispersed and individualized nanofibers. The SEM image shows that the size of the nanofiber from the suspension was measured to be 20–100 nm in diameter at 40 K magnification (Fig. 4a). The structure of these resulting nanofibers were obtained as network like structure.

The TEM image of water hyacinth cellulose nanofibers after the mechanical process was shown in Fig. 4b. The sonication process has resulted to the individualization of fibers with a diameter of 25 nm and its length in few microns. From the SEM and TEM images, the diameters of the fibers were calculated using the image tool analyzer.

3.2. FTIR analysis

The FTIR spectrum of crude fibers and nanofibers from water hyacinth was shown in Fig. 5. The peak around at 3400 and 2900 cm^{-1} are due to –OH and –CH stretching vibration. In the crude fiber, the peak at 1735 cm^{-1} was observed due to either the acetyl and uronic ester linkage of carboxylic group of the ferulic and p-coumeric acids of lignin and/or hemicelluloses. This peak was disappeared in the nanofibers after the chemical and mechanical treatment. The peak at 1512 cm^{-1} was observed in the original crude fiber, it indicates the C=C stretching of aromatic rings of lignin but in the treated one it was disappeared due to the partial removal of lignin (Sain & Panthapulakkal, 2006; Sun, Xu, Sun, Fowler, & Baird, 2005; Xiao, Sun, & Sun, 2001).

The original fiber has a peak at 1637 cm^{-1} representing the adsorbed water and this peak was decreased in the nanofibers due to the removal of hemicelluloses. In the FTIR spectrum of nanofiber, the peaks observed at 1060 and 896 cm^{-1} were attributed to C–O stretching and C–H rocking vibration of cellulose structure (Alemdar & Sain, 2008).

3.3. Thermogravimetric analysis

The results obtained from thermogravimetric analysis for original untreated water hyacinth fibers and chemically treated fibers are shown in Fig. 6. The TG curves shows that the initial drop occurs between 50 and 150 °C attributed to weight loss of absorbed moisture. Due to low decomposition temperature of hemicelluloses, lignin and pectin, the untreated plant fibers began to degrade around 206 °C (Chen et al., 2011). The decomposition temperature of original crude fibers and purified cellulose fibers was found to be at 202 °C and 253 °C respectively.

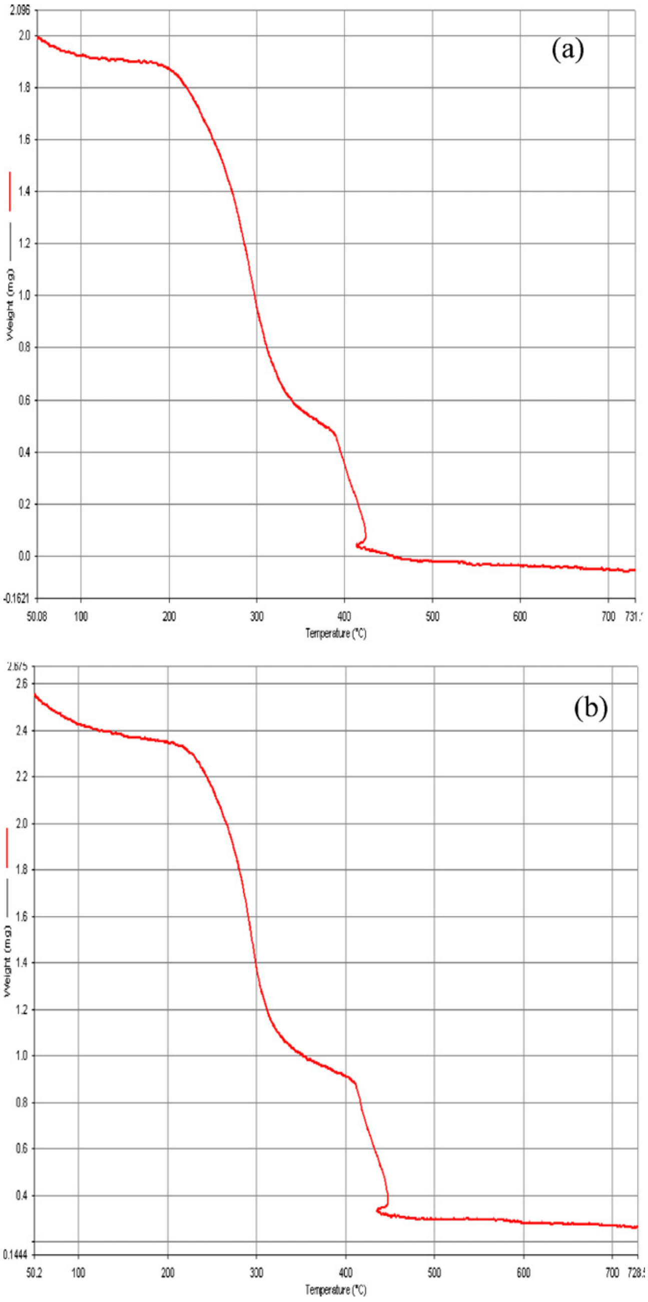

Fig. 6. TGA study of (a) original crude fibers and (b) cellulose fibers of water hyacinth.

The residues remaining in the untreated and treated fibers after heating to 500 °C constitutes the presence of carbonaceous materials. The TGA analysis showed minimum residual mass in the purified cellulose fibers probably due to the removal of hemicelluloses and lignin. The results revealed that the thermal stability of the cellulose fibers increased after the chemical treatment when compared with the original crude fibers (Alemdar & Sain, 2008; Sain & Panthapulakkal, 2006).

4. Conclusions

Cellulose nanofibers were isolated from the aquatic weed water hyacinth by a combination of chemical and mechanical treatments.

The SEM investigation revealed that the pure cellulose fibers have been obtained after the chemical treatment. The TEM analysis evaluated the isolated nanofibers are having diameter of 25 nm and its length in micrometer. The FTIR spectra confirmed the removal of lignin and hemicelluloses when treated with acidified sodium chlorite and sodium hydroxide solutions under various time intervals at appropriate temperatures. The TGA analysis revealed that the decomposition temperature of the fibers increased after the successive chemical treatments. The present investigation has highlighted the utility of the aquatic weed, which is considered as a major cause of polluting in many areas. It has also demonstrated the feasibility of producing cellulose nanofibers, which can have potential applications in the near future. Further studies will explore the applications of these nanofibers.

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