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Short communication

Isolation and characterization of crystalline, autofluorescent, cellulose nanocrystals from saw dust wastes

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ABSTRACT

Saw dust, generated as a waste by-product of the timber industry finds limited industrial applications and are mostly discarded or incinerated, causing environmental problems. This paper discusses the isolation of cellulosic nanocrystals (CNCs) from two different varieties of commercially used timber viz. *Gmelina arborea* and *Salvadora oleoides*, through a chemically engineered hydrothermal process. The CNCs derived after a series of chemical pretreatments followed by hydrothermally assisted fibrillation and subsequent neutralization, were carefully characterized for their chemical composition and microstructural attributes. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements demonstrate the fibrillation of the wood cellulosic fibers to ~18–35 nm diameter range, with nearly uniform lengths in the range of ~101–107 nm. The X-ray diffraction (XRD) spectra show the crystalline nature of the CNCs and corroborates to the spectra of known crystalline cellulosic derivatives. The photoluminescence (PL) studies showcase an interesting property of autofluorescence at ~400 nm with high quantum yields (~59%), which is attributed to the presence of fluorescent subunits identified in the FTIR spectra. The results demonstrate a simplistic method for conversion of the saw dust to high quality, fluorescent, cellulosic precursors that can find novel applications in the manufacturing, biomedical and pharmaceutical industries.

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1. Introduction

Wood is a naturally occurring renewable resource that is commercially exploited for construction, timber, paper and in wood products based industries. Chemically, wood is a biopolymeric composite of cellulose, hemicelluloses and lignin. Cellulose is a structural polysaccharide which is the major component of the biopolymers constituting the wood biomass (Moon et al., 2011). The fibrillation of plant cellulosic raw materials through mechanical and chemical processing (Chirayil et al., 2014), results in the introduction of anionically charged functional groups onto the surface of the cellulose microfibrils. This in turn, brings about a strong electrostatic repulsion between the microfibrils in aqueous environments, leading to their mechanical disintegration and the formation of nanocellulose particles (Van den Berg et al., 2007). Different extraction methods exist for step-wise breakdown of the hierarchical structure of plant derived celluloses to yield nanoscaled cellulosic materials (Moon et al., 2011; Lavoine et al., 2012). Hydrothermal treatment (steam explosion) of cellulosic precursors has been widely employed both natively and in conjunction with chemical treatments, to convert the source biomass into products of desired dimensions and functionalities (Cherian et al., 2010; Deepa et al., 2011; Abraham et al., 2013). Moreover, in the recent years nanocelluloses have garnered significant attention as nanoscaled fluorescent systems, owing to the possibility of their surface conjugation with various known fluorophores (Dong and Roman, 2007; Díez et al., 2011).

Saw dust, which is produced as a by-product of the timber based industries is generally utilized as a source for energy production. However, such processes gives rise to a significant volume of wood-ash, which has adverse environmental effects (Ban and Ramli, 2011). In the current study, we report the utilization of saw dust obtained from two different wood varieties (*Gmelina arborea* and *Salvadora oleoides*), used in the timber industry, for the development of autofluorescent cellulose nanocrystals (CNCs). These CNCs, herein designated as CNC1 and CNC2, were isolated by a chemically assisted hydrothermal defibrillation of the saw dust precursors. The isolated products were characterized by subjecting them to microstructural, biochemical and spectroscopic analysis. The results provide insights into their size, morphology, surface

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characteristics and also reveal a novel optical property, showing native fluorescence in the isolated CNCs.

2. Materials and methods

2.1. Isolation of cellulose nanocrystals (CNCs) from saw dust

Saw dust samples of *G. arborea* and *S. oleoides*, were freshly collected in separate containers from local saw mills of the Napaam area, Tezpur, India. Sulphuric acid (H_2SO_4), Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Sodium hypochlorite (NaOCl) and Acetic acid (CH_3COOH) of analytical grade were purchased from Millipore India Pvt. Ltd. The saw dust samples were washed thoroughly with distilled water for the removal of surface impurities. They were subsequently weighed (10 g) separately into a 50 ml stainless steel grinding mill container, with an internal steel surface, and loaded with 30 g of stainless steel balls (5 mm diameter). The vessel was used on the EGOMA Auriga Planetary Ball Mill (India) for milling, and each of the samples were wet milled at 500 rpm, at room temperature. The process was repeated at definite intervals till it yielded finely milled particles. The milled samples were then subjected to chemical processing by soaking in 2% NaOH solution for a period of 14 h. They were successively autoclaved in a SS-316 Mechomine Teflon lined-autoclave (India) under 137,895 Pa (20 Psi) at a temperature of 210 ± 5 °C, for a period of 8 h. The steam exploded saw dust samples were cooled to room temperature and then bleached with a solution containing a predetermined amount of NaOH, CH_3COOH and NaOCl. Further they were treated in a 10% HCl solution and sonicated for 2 h at 40 °C using a Sartorius Labsonic M Ultrasonic Homogenizer (Germany) at an operating voltage of 240 kV and frequency of 24 kHz, to finally yield cellulose nanocrystals (CNCs). The samples were finally washed to neutralize the pH. The as-prepared nanocellulosic samples isolated from *G. arborea* and *S. oleoides* were termed as CNC1 and CNC2 respectively. A schematic representation of the isolation procedure is provided in Fig. 1.

2.2. Chemical analysis of the isolated CNCs

The chemical analysis of the native saw dust samples and the derived CNCs was carried out to estimate the total cellulose and lignin content present in the samples. Based on the Technical Association of Pulp and Paper Industry (TAPPI) standard T203 CM-09, the cellulosic content in the samples was estimated. The total lignin content present in the samples was determined in accordance to the TAPPI standards T222 OM-02 and T222 OM-11 [www.tappi.org/content/pdf/standards/subject_index_tms.pdf].

2.3. Characterization of the CNCs

The microstructural study of the CNCs was carried out through a JEOL JEM-2100 transmission electron microscope (USA). A droplet of the dilute suspension of the CNCs was deposited on a carbon-coated copper microgrid (400 mesh) and it was allowed to dry under vacuum, prior to the transmission electron microscope (TEM) analysis. Dynamic light scattering (DLS) and Zeta potential measurements were employed to observe the variation in the size distribution of the isolated CNCs and their surface charge in aqueous dispersion. These measurements were carried out on a Malvern Zetasizer Nano S90 (UK) Dynamic Light Scattering system operating at a wavelength of 633 nm with a scattering angle of 90°, under a constant temperature of 25 °C. The average hydrodynamic diameter and the size distribution of the samples were obtained in the fully automated mode of Zetasizer Nano S90. Prior to the size and zeta analysis, the samples were diluted to 100× using deionized water and sonicated for 35 min (Sartorius labsonic M, 230 V, 24 kHz, Germany). X-ray diffraction (XRD) was used to obtain the diffractograms and calculate the crystallinity of the isolated CNCs. The powder X-ray diffraction patterns of the native saw dust and the processed CNCs were obtained from a RIGAKU Miniflex Benchtop X-ray Diffractometer (Japan) using Ni filtered Cu Kα radiation (λ = 1.5406 Å) at the operating voltage and current of 40 kV and 15 mA respectively. The FTIR spectra of the processed CNCs and their native saw dust precursors were recorded on a Perkin Elmer Spectrum 100 Optica FT-IR Spectrometer (USA). A few milligrams of the samples were pestled with KBr and pelletized and the IR spectra of the pellets were recorded at a wavelength range of 650–4000 cm^{-1}. The thermal stability of the native samples and the CNCs were comparatively estimated by TGA (Thermogravimetric Analysis) measurements using a STA 6000 Simultaneous Thermal Analyzer from Perkin Elmer (USA). The spectra were recorded under an ambient nitrogen atmosphere by gradual heating of the samples from room temperature to 800 °C at a heating rate of 20 °C min^{-1}. The isolated CNCs were also subjected to UV–vis absorbance studies using a Shimadzu-UV2450 UV-Vis spectrophotometer (Japan) with the average extinction coefficient obtained at a sample concentration of 0.05 g L^{-1} in deionized water. The photoluminescence spectra of the aqueous dispersion of the CNCs, was obtained using a Perkin Elmer LS-55 fluorescence spectrophotometer (USA) and the quantum yields were calculated.

3. Results and discussion

The high pressure homogenization treatment of the saw dust samples, brought about by the steam explosion and subsequent chemical processing, resulted in the significant fibrillation of the native samples. This yielded fibrillar cellulose nanocrystals (CNCs) as seen in the TEM images of CNC1 and CNC2 (Fig. 1a and c). The CNCs were observed to have an entwined fiber-like morphology with an average width in the range of 20–30 nm for CNC1 and 18–35 nm for CNC2 respectively. Since the TEM analysis provides localized information on the dimensions of the CNCs that have been dried and processed, the dynamic light scattering (DLS) technique was used to analyze their behavior in the dispersed state. A major limitation with this technique is that it measures the translational diffusion of the particles in dispersion, considering them to be spherical in shape. However, the hydrodynamic diameter, indicating the size of these particles, can be obtained from such measurements (Boluk and Danumah, 2014). The average hydrodynamic diameter of the CNCs estimated by the DLS technique was found to be in the range of 107.48 ± 2.6 nm for CNC1, and 101.36 ± 2.3 nm for CNC2 respectively (Fig. 1b and d). These values, appear very close to length of the entwined CNCs observed in the TEM images. Such minor variations with respect to the length of the particles have been observed previously, when both the techniques were used for CNC size estimations (Fan and Li, 2012; Kos et al., 2014). We may infer from the above data that the DLS measurements were able to give a simple, yet fast estimation of the average CNC length in dispersion, while the TEM images gave the dimensions of the width of CNCs, which cannot be otherwise obtained through DLS measurements (Kos et al., 2014). The DLS measurements are however are incomplete without the estimation of the zeta potential, which indicates the stability of a colloidal dispersion (Greenwood and Kendall, 1999; Hanoar et al., 2012). The zeta potential of the CNC1 was observed to be in the range of −34.28 ± 1.26 mV and that of CNC2 was −30.14 ± 1.17 mV, respectively (Fig. S1a and S1b). From the above data it may be inferred that the colloidal dispersions of the CNCs are stable (Greenwood and Kendall, 1999; Hanoar et al., 2012) (Fig. 2).

The XRD diffractograms (Fig. 3a) of the isolated CNCs show the presence of the peaks (1 0 1), (1 0 1¯) and (0 0 2) corresponding to

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