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Strategy Towards Active Food Packaging Material From Cellulose Nanoparticles and its Characterization

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Abstract: The utilization of agro-industrial wastes such as sugarcane bagasse (SCB) as a source of cellulose has influenced a wide range of interest in various applications such as food packaging, drug delivery, paper production, etc. Owing to the rich source of cellulose in SCB, the nanoparticle was prepared efficiently. The pure form of cellulose was isolated from SCB by eliminating the remaining components such as hemicellulose and lignin by treating SCB with a soluble base and a bleaching agent. Cellulose nanoparticles were synthesized from the purified cellulose by acid hydrolysis using H_2SO_4 followed by dialysis to remove sulfate ions and attain neutrality. The obtained nanoparticles were characterized using FTIR spectroscopy that helped to confirm the exclusion of lignin and hemicellulose. The crystalline nature of the cellulose nanoparticles (CNPs) was confirmed using X-Ray Diffraction (XRD). The morphology of CNPs was studied by scanning electron microscopy (SEM), and the particle size of CNPs was found to be 189 nm by particle size analysis (PSA). Further, this study proved the nanomaterial preparation from agro-wastes can be utilized to develop food packaging film in food industries.

Keywords: sugarcane bagasse; cellulose nanoparticles; FTIR; XRD; SEM; PSA.

1. Introduction

Sugarcane bagasse, an abundant fibrous agro-industrial waste, is produced in sugar production. In India, about 80 million metric tons (MMT) bagasse are generated, among which 70 MMT are utilized in steam and power industries, while the remaining are left unemployed [1]. The second leading producer and consumer of sugar worldwide is India and is the most important producer of sugarcane after Brazil [1-3]. The constituents of sugarcane bagasse are 40–50% crystalline cellulose, which is added up with hemicelluloses and xylose, arabinose, galactose, and mannose that are amorphous in structure [4, 5]. The remaining components in SCB include lignin, mineral, wax, and so on [6, 7].

Cellulose is one of the most profuse biodegradable polymers present in nature that is continually restored due to photosynthesis. It is the utmost important component of almost all the plants, including cotton, wood, hemp, cereal straws, sugarcane bagasse, pomaces of fruits and vegetables, and so forth [8]. Nanocellulose can be utilized in several areas, including papers, biocomposites, emulsion and dispersion technology, oil recovery, medical, and cosmetic applications, but the food applications were initially acknowledged as an exceedingly

captivating application field for nanocellulose because of the rheological nature of the nanocellulose gel [9]. Cellulose nanocrystals are needle-like particles of cellulose that are crystalline in nature with a dimension equal to or lesser than 100 nm [10].

There are various studies reported on cellulose extraction and nanocellulose preparation from agro-wastes like cassava peel [11], *Calotropis procera* biomass[12], Potato peel [13], Sesame husk [14], Jack fruit peel [15], pineapple leaf [16], garlic skin [17], and sugarcane bagasse [8], [18, 19]. Though few reports are available on cellulose nanofibres from sugarcane bagasse, a local cultivar was used in this study. Therefore, the primary purpose of the present study is to employ SCB as a source for extraction of cellulose and conversion into nanoparticles, which is an effective strategy towards packing of food materials and their characterization by FTIR, XRD, SEM, and PSA. The characterized nanoparticles can be used to develop food packaging film in future studies.

2. Materials and Methods

2.1. Sample collection.

SCB, a locally available agro-waste, was collected from a local sugarcane juice shop in Coimbatore, Tamilnadu, India. The collected SCB was cleaned and air-dried for about 1 week. Then, the dried SCB was cut into tiny pieces and then ground into a powder [6].

2.2. Isolation of cellulose.

The powdered sample of 5g was dewaxed with 1:2 (v/v) of ethanol and toluene in a water bath at 75°C for 4 hours and then dried. The exclusion of lignin from the dewaxed sample was repeated three times using 1.3% $NaClO_2$ (adjusted to a pH range of 3.5 to 4 using 10% acetic acid) and then dried. The hemicellulose removal was performed by treating the delignified sample with 10% sodium hydroxide at 25°C for 17 hours under continuous stirring [18, 20, 21]. After the expulsion of non-cellulosic components from SCB, cellulose in purified form is obtained, estimated using the anthrone method [22].

2.3. Synthesis of cellulose nanoparticles.

The hemicellulose and lignin-free purified cellulose was acid hydrolyzed by refluxing it with 64% (w/w) of sulphuric acid in a ratio of 1:10 g/mL under vigorous stirring at 45°C. After 1 hour, the hydrolysis was quenched by adding 10 folds of distilled water. Eliminating the acidic solution, centrifugation of the sample was performed for 15 minutes at 10,000 rpm, and the supernatant was discarded. Dialysis of the sample was done using distilled water as a solvent for 5–7 days to attain neutrality and exclude sulfate ions [23]. The mixture obtained after dialysis was then homogenized to produce nanocellulose by sonicating for 10 minutes [24].

2.4. Characterization studies.

2.4.1. FTIR analysis.

An FTIR analysis was performed for the untreated and treated SCB to confirm the elimination of non-cellulosic components using FTIR (Shimadzu, Japan). The spectra were

taken in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}, and the reading was observed using %Transmittance.

2.4.2. Analysis of crystallinity by XRD.

An XRD analysis was performed for the obtained CNPs using an X-ray diffractometer (Empyrean, Malvern Panalytical) with Cu Kα radiation source of wavelength 1.54 A operating at 45kV voltage and 30 mA current. The degree of crystallinity of the CNPs was derived using the formula described by Rabek [25]:

$$RC\ (\%) = (Ac/\ (Ac + Aa)) \times 100 \quad (1)$$

where, *Ac*- is the area of crystalline peak and *Aa* is the area of the amorphous peak on the X-ray diffractogram.

The average size of the crystals of CNPs was calculated using the following Scherer formula:

$$\tau = K\lambda/(\beta \cos\ \theta\ ) \quad (2)$$

where, λ denotes the wavelength of the X-ray used (1.54 A˚), θ is the diffraction angle, K is the shape factor (0.94), and β is the full width at half maximum of the peak (FWHM) [26].

2.4.3. Analysis of morphology by Scanning electron microscopy (SEM).

The morphological analysis of prepared cellulose nanoparticles from SCB was performed using scanning electron microscopy. SEM micrographs of surfaces were taken using a scanning electron microscope (CAREL ZEISS - EVO 18). The samples were coated with gold by the sputtering technique.

2.4.5. Particle size analysis by dynamic light scattering (DLS).

The particle size of the prepared cellulose nanoparticles was measured by dynamic light scattering (DLS) using Micromeritics, Model: Nano plus. The conditions maintained for measurement: refractive index of water, 1.33; viscosity, 0.8878 (cP); and temperature, 25°C.

3. Results and Discussion

3.1. Isolation of cellulose and nanoparticles preparation.

In this work, cellulose was isolated in purified form from SCB, and it was converted into nanocellulose by acid hydrolysis. Removal of wax from SCB before chemical treatment using the mixture of toluene and ethanol leads to a better yield of purified cellulose [27]. After dewaxing the sample, the wax content in the SCB was removed, which was ensured by the reduction in the sample weight from 5 ± 0.2 g to 4.5 ± 0.2 g. Delignification using sodium chlorite is generally a bleaching process, which turns the sample white, indicating the exclusion of lignin. Treating the delignified sample using alkali paves the way for hydrogen bond breakage, resulting in higher hemicellulose removal [28], as shown in Figure 1. Whitening the material post-purification confirms that a great quantity of the non-cellulosic components present in the beginning was eliminated [16]. The yield percentage of purified cellulose was

found to be 44 ± 2.3%, and the cellulose concentration in the purified sample was estimated to be 1.5 mg/mL.

After cellulose was prepared, acid hydrolysis was performed to generate cellulose nanoparticles from purified cellulose. Further, to break the sample into linear fragments, it was homogenized using a sonicator. After sonication, the obtained slurry revealed a remarkably high viscosity. A similar observation has been stated by Dos Santos *et al*. (2013) [16].

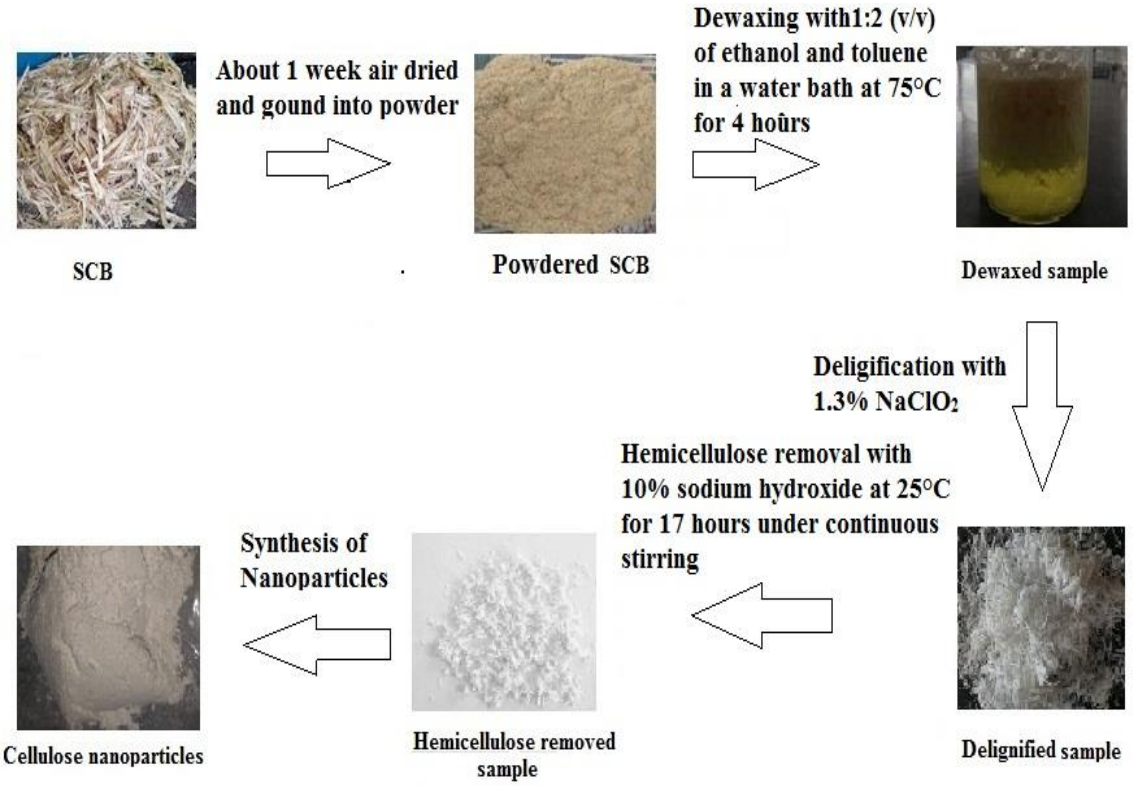

Figure 1. Schematic steps involved in the preparation of CNPs from SCB.

3.2. Characterization studies.

3.2.1. Fourier Transform infrared spectroscopy (FTIR).

FTIR has been broadly used in research based on polysaccharides like cellulose because of its accurate prediction of chemical changes that arise after the treatment using the chemical method. The changes that occurred in the structure of SCB were observed by comparing the FTIR spectrum of SCB pre- and post-chemical treatment, as shown in Figure 2. The peaks between 3200 and 3400 cm^{-1} were because of the O–H stretching of the hydrogen-bonded hydroxyl group of lignin and cellulose [29]. The strong peaks at 1726 $cm^{-1}$and 1242 cm^{-1} were observed in untreated SCB, which denotes the acetyl uronic ester groups of hemicelluloses, the ester linkage of the carboxylic group of the ferulic and p-coumaric acids of lignin or hemicelluloses. These peaks were not observed in the cellulose spectra because of the elimination of non-cellulosic compounds by chemical treatments [30], thereby depicting that the cellulose molecular structure remains unaffected even after acid hydrolysis.

3.2.2. X-ray diffraction (XRD).

The XRD was done to examine the crystalline structure of CNP produced by the chemical method. The sample showed a higher peak intensity at about 2θ = 22.19, which is

interrelated to the cellulose crystal structure. The degree of crystallinity and crystal size of CNPs was derived from the X-ray diffractogram (Figure 3).

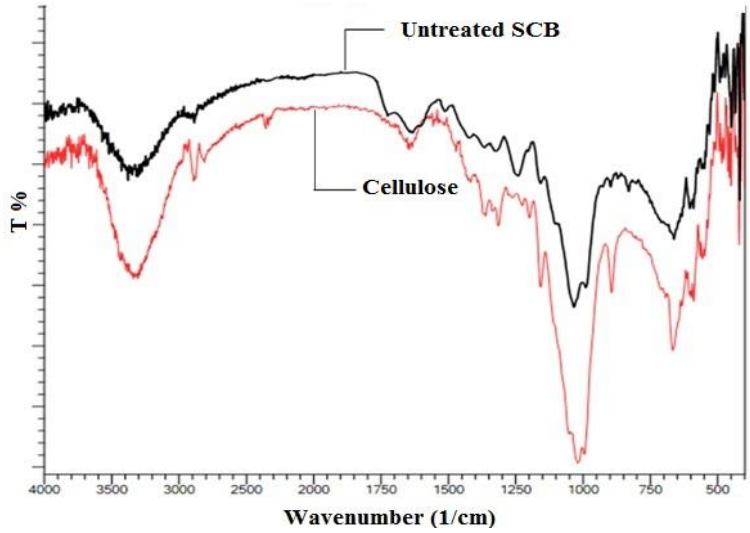

Figure 2. FTIR spectrum of ground untreated SCB and cellulose.

Based on the method described by Rabek (1980), in equation (1), the degree of crystallinity of CNPs was observed to be 88.3% that proving the exclusion of amorphous properties of cellulose [31]. Similar to this study, the rise in crystalline nature has also been observed by Said Azizi-Samir *et al*. (2004) [32], Tang *et al*. (1996) [33], and Mandal and Chakrabarty (2011) [4]. Using the Scherrer equation (2), the crystal size of CNPs was identified to be 30 nm approximately. Since this material has high crystallinity, it can be concluded that CNPs have great potential to be used as reinforcement agents to produce nanocomposites and for various applications.

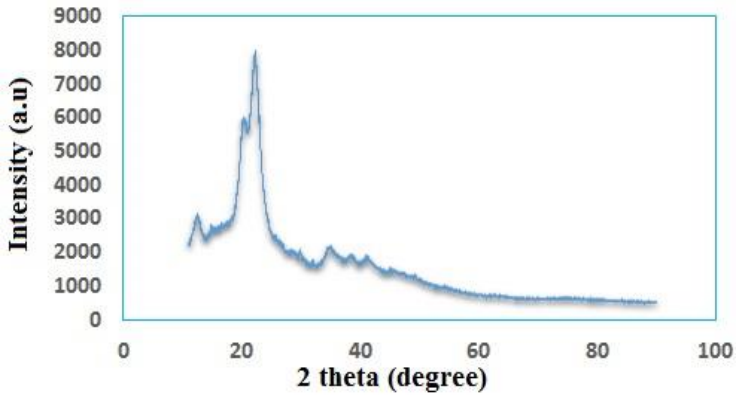

Figure 3. X-ray diffractogram of synthesized CNPs from SCB.

3.2.3. Scanning electron microscopy (SEM).

Figure 4 shows the morphology of cellulose nanoparticles prepared from cellulose fiber (Figure 4 a and b). After excluding moisture from the nanoparticles obtained, the particles get assembled into fibers of sub-microns and micrometer length [34] because of the rise in H-bonding between -OH groups present on the cellulose surface. The acid-hydrolyzed CNPs showed spherical and rectangular rod-like structures. A similar observation has been described by Ramesh and Radhakrishnan (2019) [13].

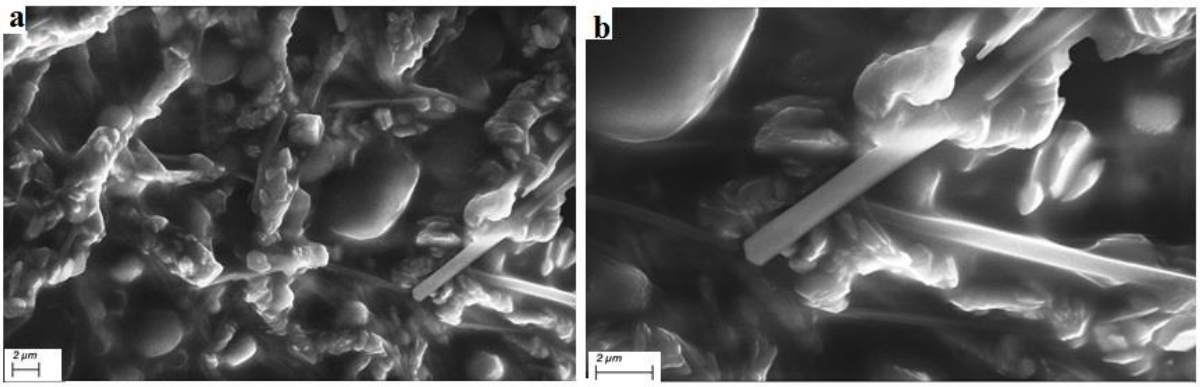

Figure 4. SEM images show the morphological analysis of CNPs from SCB at different magnifications.

3.2.4. Particle size analysis (PSA).

The DLS method was used to analyze the size distribution of the CNPs, synthesized from SCB. As shown in Figure 5, the size distribution signifies that the nanoparticle comprises particles in nanometers. The cellulose nanoparticle diameter was observed to be 189 nm. The smallest size of the particle is approximately 52.10 nm. This intensity distribution depicts that the particle size after the chemical treatment is 90% lesser than 1056.80 nm, which ascertains that the particle lies in the nanometric range.

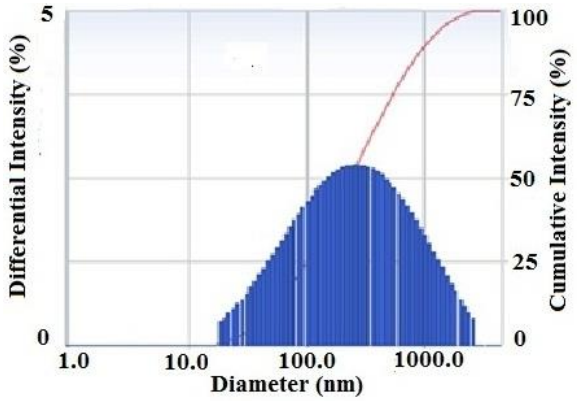

Figure 5. Particle size distribution of CNPs from DLS method.

4. Conclusions

This study affirms that cellulose can be acquired from agro-industrial wastes like sugarcane bagasse. The elimination of compounds other than cellulose from SCB was performed effectively using a bleaching agent, sodium chlorite, and an alkali, sodium hydroxide. After hydrolysis using sulfuric acid, further purification of cellulose nanoparticles was done by centrifugation and dialysis. The acid-hydrolyzed cellulose showed a higher degree of crystallinity, which was confirmed by XRD and proves this material can be used as reinforcement agents for the manufacturing of nanocomposites. The obtained SEM images and intensity distribution of CNPs depict that the size of the obtained particle is in nanoscale. As a result, it proves to be valuable in the employment of SCB for CNP preparation and its applications in food packaging film development.

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Conflicts of Interest

The authors declare no conflict of interest.

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