



Synthesis and Characterization of Nanocellulose fibers from Ragi Stalk by Acid Hydrolysis

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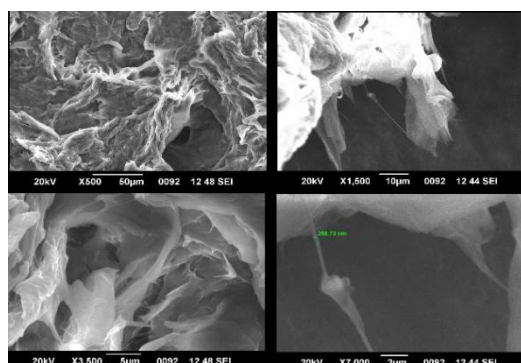
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ABSTRACT

The present research emphasizes lignocellulosic material such as Ragi Stalk or Eleusine Coracana was converted into cellulose by pretreatment with NaOH and NaClO₂ Solution. In addition, the cellulose obtained was transformed into Nanocellulose (NC) using acid hydrolysis, ultrasonication, and centrifugation. XRD (X-ray diffraction), SEM (Scanning Electron Microscopy), FTIR (Fourier transform infrared spectroscopy), and TGA/DTA (Thermogravimetry and Differential Thermal Analysis) are used to characterize the nanocellulose that has been synthesized. According to the FTIR findings, the chemical structure of cellulose synthesized from these agricultural biomasses was not affected by the synthetic approach. According to SEM studies, the synthetic procedure employed affects the morphology/surface topology of synthesized nanocellulose. XRD studies reveal the crystalline and semi-crystalline nature of the synthesized nanocellulose. TEM monographs illustrate the surface structure and size of the synthesized nanocellulose ranging from 9 to 14 nm. The thermal stability of nanocellulose is revealed by TGA/DTA studies and the obtained nanocellulose shows superior thermal stability up to 342.4°C.

Graphical Abstract:



SEM Image of AH-RSNC.

Keywords: Ragi Stalk, Acid hydrolysis, Lignin, Cellulose, Nanocellulose.

INTRODUCTION

Much research has been done in recent years to categorize materials that can be produced on a nanoscale while yet having the ability to lead civilization sustainably [1-2]. Cellulose is a biopolymer found naturally in plant cells such as wood and cotton and it is the most prevalent polymer in nature besides the primary ingredient of tree and plant cell walls. The highest cellulose content was found to be in cotton among all the plants and it is about 90% cellulose when compared to wood which contains up to 40–50% cellulose. The bast fibers, such as flax, hemp, or ramie, comprise 70–80% cellulose. Aside from these, cellulose is found in various bacterial species, algae, and sea tunicate [3]. Hence, it makes a considerable green nanotechnology material. Any crop containing lignocellulose, which comprises a set of plants, can be used as a precursor material for cellulose production. For nanocellulose synthesis, agricultural and wood waste are used as raw materials. Source materials for nanocellulose extraction from parent cellulose have included olive tree biomass, cotton linter, cereal straws, banana plants, and other materials [4].

Cellulose is a semi-crystalline polycarbohydrate consisting of anhydroglucose units (AGU) linked by chemical β -1,4-glycosidic bonds. Two repeating AGU having a “chair” conformation are shown in figure 1. This also includes the carbon atom numbering scheme. There are three hydroxyl functional groups in each of these units one primary and two secondary groups. Owing to the equatorial position of the hydroxyls, the AGU can form internal hydrogen bonds i.e between the hydrogen atom of the C-3 hydroxyl group of one unit and the atom of the ring oxygen of the adjacent units [5-6].

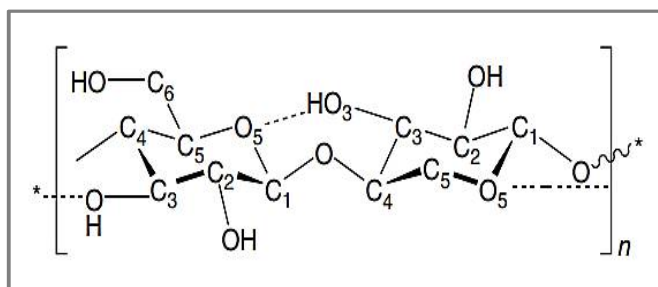


Figure-1. Repeating Unit of Cellulose Chain.

Internal hydrogen bonds hinder glucopyranose rings from freely revolving around chemical glycoside bonds, increasing the stiffness of the cellulose chain [7]. Due to a strong intramolecular and intermolecular hydrogen bonds system of intramolecular and intermolecular hydrogen bonds, crystallites are orderly organized, stiff, and strong cellulose components that are unattainable to water and some chemical reactions. Nanocrystalline amorphous regions with relatively weak hydrogen bonds, on the other hand, contribute to cellulose materials' greater hydrophilicity and accessibility. This biopolymer may establish hydrogen bonds due to the presence of (-OH) hydroxyl groups, making it a strong biopolymer [8]. Cellulose is a semi-crystalline polymer that undergoes both amorphous and crystalline processes [9]. Nanocellulose is a new shape for this ancient and necessary natural polymer (NC). Over the years, Nanocellulose is an inimitable and natural compound extracted from native cellulose using different extraction methods. Nanocellulose is gaining popularity because of its unique surface shape and chemistry, superior physical and chemical strength, and plenty of hydroxyl groups for modification. Furthermore, its substantial biological features, including biodegradability, biocompatibility, and non-toxicity, as well as its environmental friendliness, make it stand out in nanoengineering and nanomanufacturing. It's been used in a variety of applications, including sensing devices [10-11]. CNCs (cellulose nanocrystals) are natural materials that can be

used in a variety of applications. CNC is widely used in the paper and pharmaceutical industries. The various modifications of cellulose nanocrystals have been investigated. Nanocellulose is dispersible in multiple solvents due to a simple chemical modification of the cellulose surface. A strong acid approach is used to hydrolyze the cellulose obtained during the isolation process into nanocellulose [10]. Nanocellulose is used to make emulsions, packaging, bio-medical devices, and rheology modifiers like hydrogels used in biomedicine, biocomposite films, supercapacitors, and xerogels [11-17]. These applications demonstrate the potential of nanotechnology in the production of cellulose from lignocellulosic biomass.

Lignin, hemicellulose, and β -Cellulose are all known components of lignocellulosic biomass. Nanocellulose is made from β -Cellulose, which is made from lignocellulosic material that has been pretreated, and then the lignin was removed using an alkali treatment. The bleaching method removes hemicelluloses [17]. The mechanical and chemical techniques can both be used to make nanocellulose from cellulose. The mechanical process involves the process of intensified ultrasonication or high-pressure homogenization and the chemical process involves AH (Acid Hydrolysis), IL (Ionic Liquid), and TEMPO (2, 2, 2, 6,6-tetramethylpiperidine-1-oxyl) [18-21]. Acid hydrolysis is highly regarded for its ability to hydrolyze cellulose, particularly in the amorphous region. This approach has been used since 1990 and comprises the use of two acids i.e hydrochloric acid (HCl) and sulphuric acid (H_2SO_4). When nanocellulose is hydrolyzed in acid, the amorphous zone is preferentially degraded, resulting in cellulose nanocrystals (CNC) with a rod-like shape and crystalline nature retained [22].

Natural nanocelluloses derived from HCl and H_2SO_4 are distinct. This method removes the amorphous region of cellulose, resulting in a structured Cellulose Nano Crystal (CNC) [23, 24]. The NC obtained has high crystallinity and a diameter of less than 20 nm [25, 26]. For example, nanocellulose synthesized using HCl is deficient in surface charge and subject to electrostatic repulsion. When nanocellulose is produced from H_2SO_4 , a colloidal suspension is obtained [27]. When compared to the above-mentioned methods, acid hydrolysis of cellulose is more convenient in terms of time, cost, and accessibility of acid. Thus, in the current work, an acid hydrolysis technique was used to synthesize nanocellulose from naturally occurring agricultural bio-waste such as Ragi stalk, alleviating the strain on the agricultural sector in India to use natural feedstock. Numerous studies have investigated the utilization of mechanical treatment methods such as sonication, high-speed blender, high-pressure homogenization, ultrafine grinder, and ball mill to generate nanoscale fibers [28]. This procedure, however, is inefficient at separating hemicellulose, cellulose, and lignin. Sonication and chemical treatment can be used in conjunction to produce pure CNC. There are a number of methods for producing pure cellulose fibers, but sonication has been found to be the easiest of them all. Pure CNCs can be produced by using sonication and chemical treatment. To create pure Cellulose fibers, the sonication approach has been found to be the easiest mechanical treatment to use in conjunction with conventional chemical treatments [29, 30].

Biomass derived from farming the raw material employed in this research to isolate nanocellulose by acid hydrolysis using Ragi Stalk. The functionality, crystallinity, surface morphology, and thermal stability of all synthesized nanocellulose were examined using FTIR, XRD, SEM, TEM, and TGA/DTA. In this study, we have recorded the sonication effect on the crystalline structure of the nanocellulose which was not emphasized more in previous research. The nanocellulose finds valuable applications in the field of Photocatalysis, paper semiconductors, and nanocomposites as building materials. Hence this method gives a new insight to establish the prospective applications of nanocellulose in the field of science and technology [31-34].

MATERIALS AND METHODS

Lignocellulosic materials like agriculture biomass were collected from farmlands in and around Davanagere, Karnataka, India. Sulphuric acid (H_2SO_4), Sodium chlorite ($NaClO_2$), Acetic acid

(CH₃COOH), and Sodium hydroxide (NaOH), were purchased from Qualigens and Merck chemicals. All compounds were utilized as such, with purity ranging from 98.0 to 99.0 percent.

Synthesis of cellulose: The procured lignocellulosic material from agricultural biomass such as Ragi Stalk was thoroughly washed and allowed to expose for sundry for one week then dried in a hot air oven, sieved into fine powder, the powder again dried in hot air oven till it gives constant weight. An appropriate measure sample was treated with 5% NaOH solution for 3-4 h by maintaining a temperature of 90-100°C with continuous stirring using a magnetic stirrer. The isolated cellulose residue was filtered until it reached a neutral pH with distilled water. The obtained mass is then washed with ether to make it moisture free, dried, and stored for further process.

The Bleaching was performed on the material obtained following alkali treatment by treating it with 5% NaClO₂ solution for 3-4 h by maintaining acidic pH with glacial acetic acid at 85-110°C. By washing with distilled water, any remaining residual lignin was eliminated. After that, the filtration of cellulose was done repeatedly with deionized water before being brought to a neutral pH. Then this was oven-dried for one day or till it gives constant weight and processed for further preparations. Figure 2 describes the detailed scheme of acid hydrolysis.

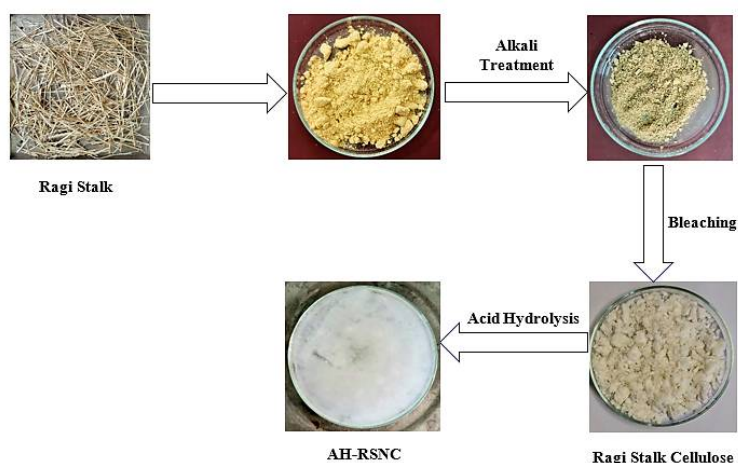


Figure 2. Acid Hydrolysis Scheme.

Synthesis of nanocellulose from acid hydrolysis: One of the most prominent ways of obtaining nanocellulose from cellulosic materials is acid hydrolysis. The acid may easily hydrolyze the disordered sections of cellulose chains, leaving the orderly parts intact. To break the glycoside bonds in cellulose, a strong acid such as H₂SO₄ or HCl is usually used. Acid hydrolysis is a multi-step process. Under monitored conditions such as concentration of acid, reaction time, temperature, and acid to cellulose ratio. Addition of water to stop the acid hydrolysis process and upon subsequent centrifugation, dialysis to completely remove free acid molecules. Sonication forms a stable nano-cellulose suspension followed by drying of the suspension yields solid nanocellulose [35-37]. This follows the mechanism shown in figure 3. To efficiently precede the hydrolysis reaction, water molecules and acid H⁺ ions must infiltrate the cellulose fiber throughout this process. Otherwise, only the cellulose surface is affected by hydrolysis. Acid catalyzes the breakdown of long cellulose chains into shorter chain oligomers, which are then degraded by the acid. The hydrolysis of cellulose produces conjugated acid, which begins with an acidic proton and oxygen reaction that links two glucose units together. After the C–O bond is cleaved, the conjugate acid is broken down to the cyclic carbonium ion, which adopts a half-chair conformation. The rapid addition of water causes the release of free sugar and proton. The intermediate carbonium ion forms faster at the end of the polysaccharide chain than it does in the middle [38].

The conventional acid hydrolysis procedure was used to synthesize each sample. 1g cellulose sample was added with 45cm³ H₂SO₄ (55% w/v), and the aliquot mixture was kept for hydrolysis between 40-45°C for about 90 minutes with continuous stirring. Ice cold deionized water was poured to minimize hydrolysis. The resultant mass obtained was repeatedly washed with distilled water till it reaches neutral pH followed by ultrasonication and centrifugation with 4000-5000 rpm for about 30-45 minutes to obtain AH-RSNC. They are kept in the refrigerator until needed. The yield of nanocellulose produced by this process was determined to be between 86 and 90%.

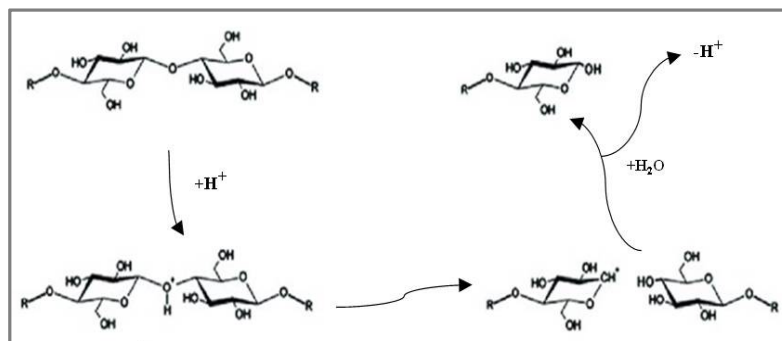


Figure 3. Mechanism of Acid hydrolysis.

Characterization: Thermo Nicolet iS50 was used to record the FTIR of Cellulose, AH-RSNC. The samples were pressed into thin pellets after being blended with KBr powder. The wavelength range of the sample was measured from 4000 cm⁻¹ to 400 cm⁻¹. The Bruker D8 Advance Diffractometer was used to record the XRD data. The peak heights of the crystalline and amorphous zones are measured, and the crystallinity index (CI) was computed using Scherer's formula, with a step size of 0.02. SEM (Scanning Electron Microscopy) images were captured with the Jeol 6390LA/ OXFORD XMX N instrument, which had an acceleration voltage range of 0.5 to 30 kV. The images were captured using a secondary electron (SE) detector. TEM images were recorded with 200 kV, LaB6 electron gun of point resolution 0.23 nm, lattice resolution 0.14 nm. The Perkin Elmer STA 6000 instrument was used for TGA (Thermogravimetric Analysis) and DTA (Differential Thermal Analysis).

RESULTS AND DISCUSSION

Nanocellulose (NC) is a biopolymer made from biodegradable plant sources that can be produced organically. NC is used in a variety of industries, including packaging, biomedical, and biocomposite preparations. In the present study, Nanocellulose was extracted from agricultural biomasses using the Acid hydrolysis method, which included pretreatment with alkali and bleaching. The synthesized NC's chemical group, crystallinity, surface morphology, and thermal stability were evaluated using FTIR, XRD, SEM, TEM, and TGA/DTA examinations.

FTIR analysis: The chemical functionality of nanocellulose was examined using FTIR after various chemical treatments. FTIR of Cellulose, AH-RSNC in figure 4. Peaks can be found in two main regions: 2800 to 3500 cm⁻¹ in high wavenumbers and 600 to 1800 cm⁻¹ in lower wavenumbers. The cellulose peaks can be seen in the FTIR spectral regions shown above.

The O-H stretching vibrations of the hydrogen-bonded hydroxyl groups in the cellulose molecules are depicted by the broad absorption peaks at 3331.89 to 3335.65 cm⁻¹. The C-H and CH₂ groups of cellulose stretching vibrations were attributed to the peaks at 2893.39 and 2901.38 cm⁻¹. The H-O-H deformation vibration of absorbed water and conjugated C=O stretch vibration are responsible for the peaks at 1638.63 to 1644.34 cm⁻¹. C-H deformation was assigned to the small shoulder peaks vibrations at 1428.67 to 1428.92 cm⁻¹ (asymmetric). The O-H association band in cellulose was

attributed to the curves at 1029.99 to 1032.53 cm^{-1} . The stretching (C-O) and rocking (C-H) cellulose peaks, which corresponded to the stretching (C-O) and rocking (C-H), respectively, appeared at 1112 cm^{-1} . The cellulose, AH-RSNC peaks at 896.98 to 899.37 cm^{-1} correspond to glycosidic linkage. Out-of plane bending causes a vibrational band at 664.01 cm^{-1} , which accounts for aromatic C-H vibration in the cellulose range, implying that removal of lignin is not favored by chemical pretreatment. The aforementioned lignin vibrational peaks have decreased slightly in the AH-RSNC spectra, showing that the remaining lignin is eliminated during acid hydrolysis after Cellulose is dissolved. Chemical and ultrasonic treatments are required to separate lignin from strong hydrogen bonds in AH-RSNC. When water molecules absorb ultrasonic energy can cause more efficient cavitation, which includes the formation, expansion, and disintegration of microscopic gas bubbles. The action of the ultrasound's hydrodynamic forces on the pulp causes the cellulose fibers to defibrillate. As a result, this method produces aggregated fibrils with a wide width distribution. Some cellulose fibers have been observed to modify their crystalline structure after being subjected to ultrasonic treatment.

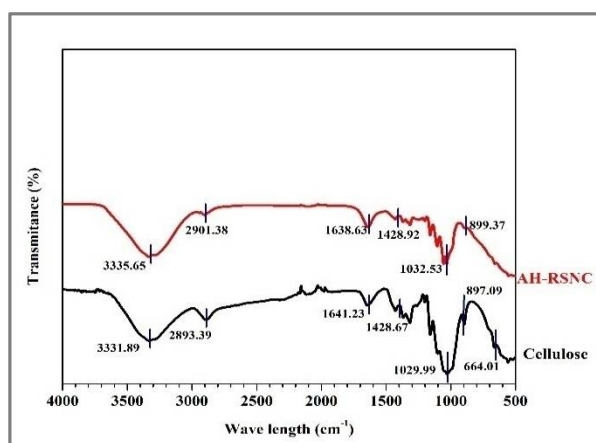


Figure-4. FTIR of Cellulose, AH-RSNC.

XRD analysis: The crystallinity of nanocellulose elucidates its thermal and mechanical properties, which is a noticeable factor. X-ray diffraction (XRD) patterns are used to study the crystallinity, thermal, and mechanical properties of three synthesized nano celluloses. Cellulose, AH-RSNC XRD patterns are shown in figure 5, with 2θ values and peak intensities founded on the synthesis method. The crystallinity of the cellulose sample peaks at $2\theta = 15.5^\circ$ and 22.23° . AH-RSNC exhibits crystallinity values of $2\theta = 22.23^\circ$, 29.50° , and 42.00° . AH-RSNC shows strong and intense peaks, indicating superior crystallinity. On the other hand, sonication does not affect the cellulose backbone's regular structure and it has a significantly wider peak at 29.50 . Ultrasonic cavitation affects both crystalline and amorphous regions of cellulose, implying that the crystallinity index declines and that ultrasonic cavitation affect the crystalline and amorphous parts of cellulose simultaneously hinting that crystalline regions are destroyed. As a result, the crystallinity of AH-RSNC has decreased suggesting that it is more flexible.

SEM analysis: The synthesized nanocellulose is fibrous, semi-crystalline, and fibrillar, according to the SEM monographs of AH-RSNC. The average size of AH-RSNC is between 250 and 300 nm, according to figure 6 (a,b). According to these findings, the dimensions of nanocellulose made from Ragi Stalk, have different topologies in the nanoscale dimension. As a result, synthetic approaches

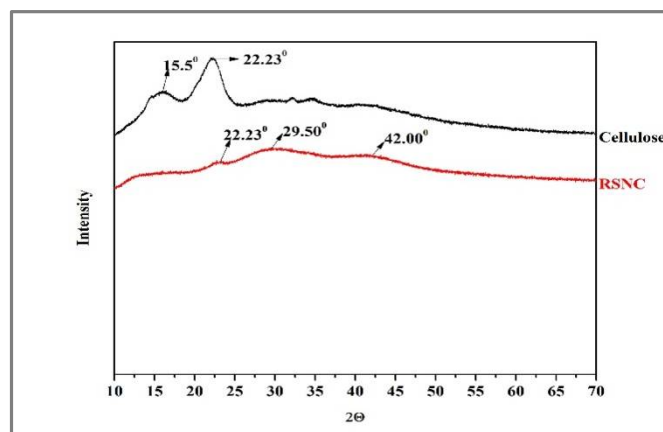


Figure-5. XRD pattern of, AH-RSNC, Cellulose.

have an impact on the size distribution and surface morphology, and most of the disordered regions of cellulose are hydrolyzed during the acid hydrolysis process, leaving the fibrous-like Nanocellulose behind, resulting in a lower aspect ratio that is ideal for polymer reinforcement. The nanocellulose obtained has a fibrous shape, which facilitates the development of value-added products.

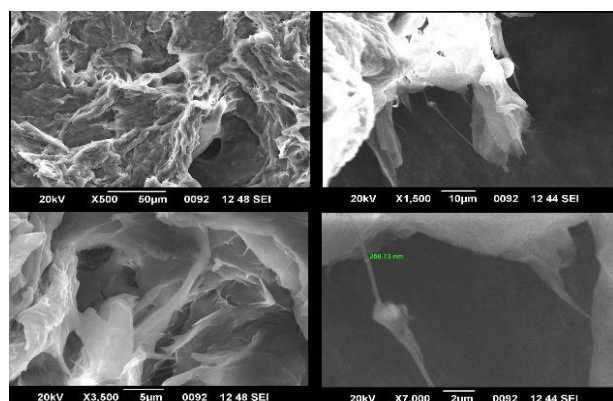


Figure-6. SEM Image of AH-RSNC.

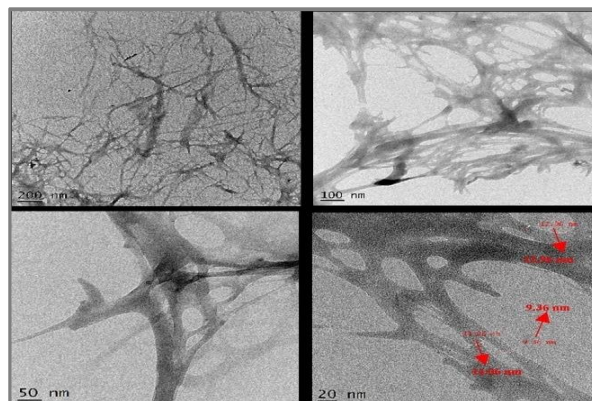
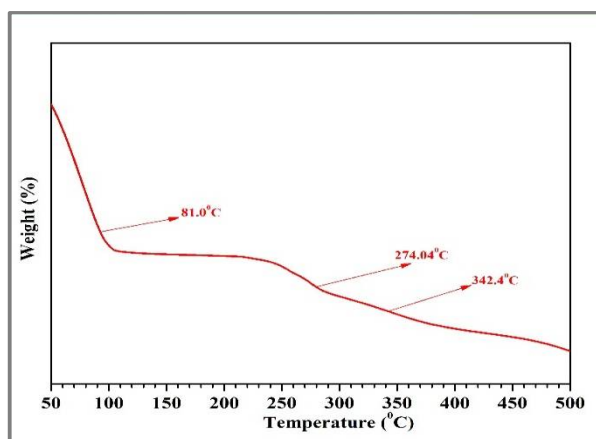
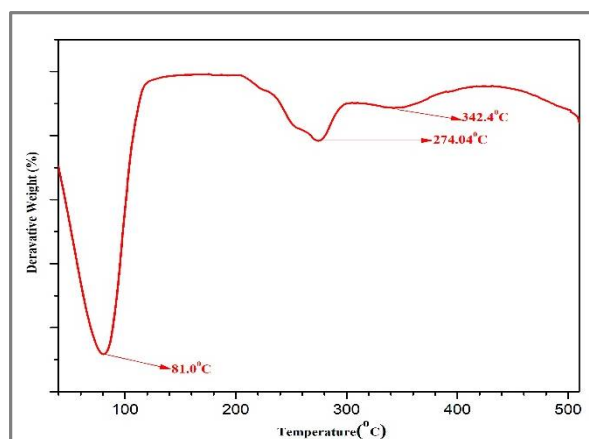


Figure-7. TEM Image of AH-RSNC fibers.

TEM Analysis: TEM images were obtained for the analysis of the internal morphology and structure of the prepared sample. Figure 7, clearly shows that the synthesized sample has nanofibrous. Nanofibers are well-separated and easily viewable. Across all the pictures, even the tendency to agglomerate can also be seen. This tendency can be attributed to the drying conditions during the preparation of samples that involved water evaporation. Figure 7 shows the TEM images of AH-RSNC have a long elongated fibrous nature, with an average diameter of 9-14 nm.

TGA/DTA Analysis: The thermal stability of the AH-RSNC was elucidated by using TGA, and the DTA curves are shown in figure 8 and figure 9 respectively. The temperatures at which the three-stage of nanocellulose degrade are as follows: This is shown in the LHS of the DTA curve as small troughs. AH-RSNC shows major weight loss at 81°C, 274.04°C, and 342.4°C. The temperatures at which the water evaporation occurred is 81°C are shown as broad troughs. Nanocellulose degrades primarily as hemicellulose and glycosidic linkages are broken and depolymerized and it is depicted between 250-274.04°C. AH-RSNC exhibits superior thermal stability up to 342.4°C.

**Figure-8.** DTG of AH-RSNC.**Figure-9.** TGA of AH-RSNC.

APPLICATION

As a result of considerable small dimensions, the synthesized nanocellulose can be used for dye degradation and Photocatalytic dye degradation studies because it may pose better dye removal efficiency. The nanocellulose can be used for making high strength structural nanocomposites. As a result of good thermal degradation temperature, it can be used in the manufacture of temperature retardant materials.

CONCLUSION

In the present work, nanocellulose was extracted from lignocellulosic materials like agricultural biomass Ragi Stalk by acid hydrolysis. Analytical and morphological data were used to characterize the nanocellulose that had been prepared. The impact of synthetic methods on nanocellulose characteristics and morphology was thoroughly examined. According to the FTIR comparison analysis, the synthetic techniques have no detectable effect on the primary functional group areas of cellulose. Acid hydrolysis demonstrates there is decrease in crystallinity. The results of SEM show that synthesized nanocellulose comes as nanofibers. The crystallinity and semi-crystalline nature of nano cellulose were depicted by XRD. TGA/DTA analysis shows that the commencement of acid hydrolyzed cellulose degradation is at 81°C, as indicated by the strong troughs in the DTA curve. RSNC has shown good thermal stability. The most important TGA finding is that acid hydrolyzed AH-RSNC (342.4°C) has a higher degradation temperature, indicating superior thermal stability. TEM monograph shows that synthesized nanocellulose is in the dimension of the nanoscale. This method clearly displays the nanometer-sized morphology and distribution of synthesized Ragi stalk. Furthermore, the purpose of this study is to demonstrate a viable application of synthesized cellulose from naturally accessible biomass, thereby addressing India's demand for solid waste management and minimizing chemical waste through a more realistic nanocellulose synthesis process. This research will point in a new direction for making better use of nanocellulose derived from agricultural biomass, opening the door to new nanomaterials made from value-added products. The current study's findings can be applied to water purification and thin films.

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