Original Research Article

Synthesis and Characterization of a Novel Maize Cob Based Nanocellulose

ABSTRACT

Nanocellulose is a renewable nanomaterial which has received a lot of attention due to its use in a variety of applications from biomedical field to food packaging. In this study, Nano cellulose (NC) was extracted from Maize cob, using Acid hydrolysis process. The extracted NC was characterized using PSA for particle size, FT-IR for functional groups, SEM and TEM for getting the morphology of NC. The result showed that, the synthesized NC was with a particle size of 213.5nm and a zeta potential of -34.5mV. The FT-IR analysis showed that the functional groups stretching at C-O, C=O, S=O with a wavenumber of 1216cm^{-1}, 1737cm^{-1},1365cm^{-1} in NC. The XRD analysis clearly depicts peak around 2θ = 15.80, 22.03, 26.69, 40.44 which shows the structure of cellulose. The SEM and TEM image confirmed the acid hydrolysis process, fiber defibrillation Cellulose and Nanocellulose formation

Keywords: Maize cob, alkali treatment, bleaching, acid hydrolysis, Nanocellulose

1. INTRODUCTION

Maize (*Zea mays* L.) is one of the most adaptable crops, able to thrive in a wide range of agro-climatic conditions. Maize is known across the world as the "Queen of Cereals" because it has the largest genetic production potential of all cereals. Maize is the third most important crop in India after rice and wheat. [1] reported that the overall cellulose output from biomass varied from 10^{10} to 10^{11} tonnes per year, accounting for roughly 40% to 50% of plant fibres. In India, the total amount of Maize cob waste produced per year is 5 million tonnes. Tamil Nadu generates approximately 2700 tonnes of waste per year [2]. In the twentieth century, maize became a key staple grain that was transformed into important cuisines and industrial items all across the world. The harvested maize crop is typically milled either dry or wet, as well as cleaned or conditioned, to yield maize kernels and waste residues such as maize cobs (MC). The MC is an extremely fibrous rachis made from the female inflorescence of maize ear as a by-product of maize processing. The cellulose content of maize cobs was estimated to be around 45 percent. As a result, using maize cob as a source of refined cellulose is a positive step forward. The most abundant type of renewable organic matter on earth is cellulose with has a biosynthetic production which is annually estimated to be over 10^{11} tons. It is a carbohydrate polymer composed of repeating β-D-glucose units. There are both amorphous and crystalline parts in it. Cellulose is a renewable natural polymer that comes in the form of fibre and is used to make a variety of materials and products. Nanocellulose (NC) is a new renewable nanomaterial with a wide range of uses in food, medicines, and personal care products. Alkalization, bleaching, and acid hydrolysis are all used to recover cellulose from agro-waste. These processes remove all other components from the fibre, leaving behind highly crystalline cellulose. With the help of Nano miller, Ultrasonicator, High pressure homogenizer cellulose is converted into Nanocellulose (NC) particles. This study examines the utilization of non-woody lignocellulosic biomass sources, particularly those classified as agro-waste, to create Nanocellulose (NC). Nanocellulose is cellulose with a fibre width at the nanoscale lattice that exists in many morphologies such as Cellulose Nanocrystals (CNCs), Cellulose Nanofibrils (CNFs), or Cellulose Nano Whiskers (CNWs), and Bacterial Nanocellulose (BNC). Nanocellulose is a biologically innovative substance that is continuously being researched for novel applications.NC materials are gaining popularity due to their appealing and great attributes such as abundance, high aspect ratio, enhanced mechanical properties, renewability, and biocompatibility. cellulose-based materials are becoming more popular as a result of their intriguing properties. The origin of the cellulose, the separation and processing conditions, as well as any pre- or post-treatments, all influence the shape, size, and other attributes of each nanocellulose type.

The nanocellulose market is expected to reach USD 783 million by 2025, according to Markets. The increasing demand for nanocellulose and the use of novel applications has prompted researchers and industry to expand their use of the materials. In this work, NC was created by acid hydrolysing corn cob powder [3]. Enzymolysis and Chlorine Oxidation

Degradation are two further mechanisms that can be used to make NC. Although these other procedures have been tried and each has its own unique effects on the resulting NC, Acid Hydrolysis is a well-known method for successfully dissolving cellulose's amorphous areas. [4] reported that Cellulose nanoparticles are remarkable materials that have applications in almost every sector of human activity. There are various advantages to scaling down lignocellulose biomass to nanocellulose. [5] reported Nano Cellulose Production Technology and Application.

2. MATERIAL AND METHODS

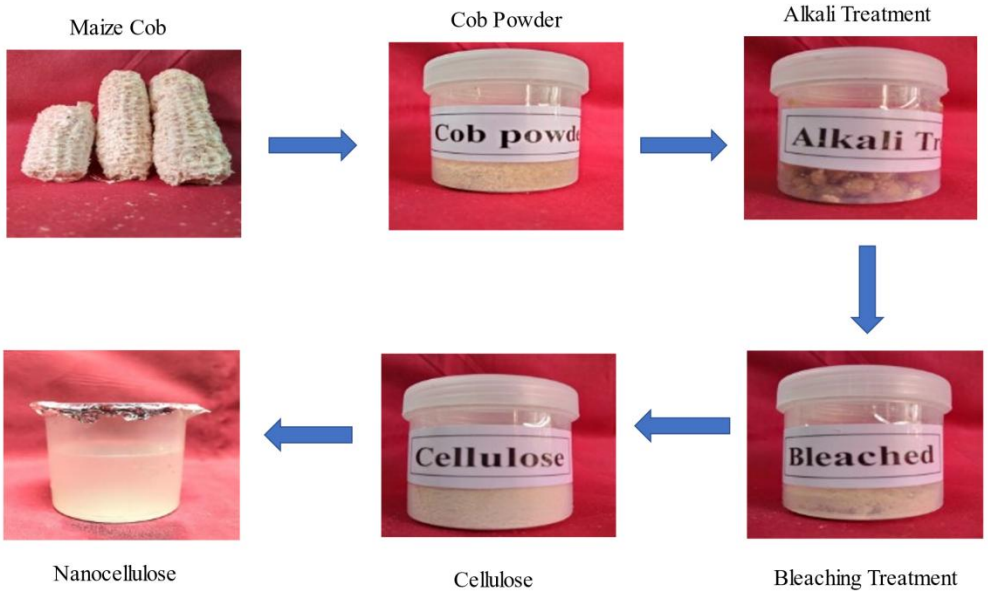
2.1 Raw Materials

The fresh Maize cobs were collected from Maize Research Station, Vagarai. Then these cobs were dried in the sunlight for two days. After two days, these cobs were grinded to a fine powder and used for the extraction of cellulose.

2.2 Extraction of cellulose from maize cob (Fig 1&2)

Maize cobs are a good source of cellulose and hemicellulose, but they also have a lot of lignin. To extract cellulose from maize cob, three major techniques were used, Alkali treatment, Bleaching, and Acid hydrolysis. In the Alkali treatment, 100g of fiber was mixed with 1L of 2% sodium hydroxide (NaOH) (purchased from Sigma Aldrich chemicals), and it was placed in an autoclave at 20 lb for 1 hour at 121°C. During this process, the lignin and other contaminants present in the cob powder were dissolved and washed with water & decanted. Next the bleaching process was done with mixing of sodium hydroxide, acetic acid, and 4% sodium hypochlorite in 1:3 ratio and kept it undisturbed for overnight. After that it was washed with water (H_2O) to remove the bleaching agent, and this process was repeated 3-4 times until the fiber color changes from brown to white. After the bleaching process followed by acid treatment, by adding 11% oxalic acid (the ratio of fiber & oxalic acid 1:4) and kept in an autoclave at 20lb for 15 minutes. At the end of the time, it was rinsed with water until the pH is back to neutral. The final product was white colored powder cellulose in micro size. [6] reported the process of alkali hydrolysis for extraction of Nanocellulose from Sugarcane bagasse.

Fig.1. Extraction of Nanocellulose from Maize Cob



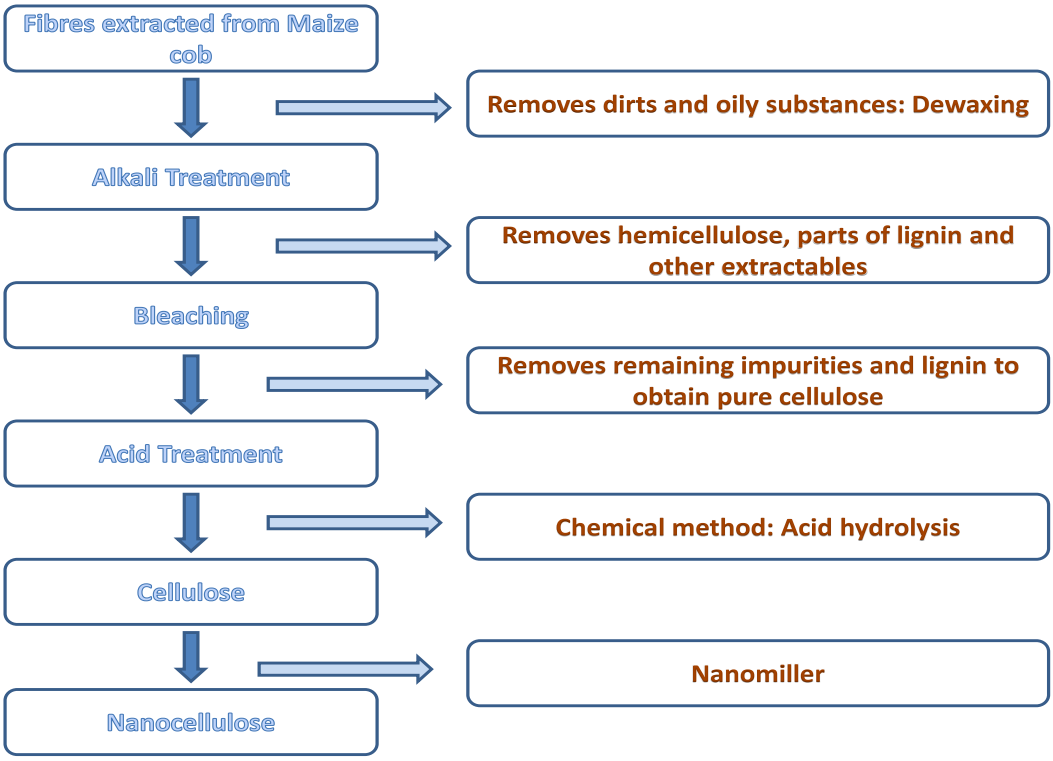


Fig. 2. Flow chart for extraction of Nanocellulose from Maize Cob

2.3 Conversion of microcrystalline cellulose into nanocellulose

The obtained microcrystalline cellulose is converted into nanocellulose using a ultra-sonication process. The cellulose suspension was dispersed using Ultrasonicator for 15 minutes with the temperature and amplitude of 45^{o}C & 27m. The NC obtained from the Ultrasonicator was characterized using different instruments. [7] reported that to separate the nanocellulose, the cellulose suspensions were sonicated for 30 minutes at 20–25 kHz with a 1000 W output power using an ultrasonic processor. [8] reported the extraction of cellulose nanocrystal from cotton by Ultrasonication process. [9] reported the Agricultural wastes derived from walnut shells are used in the synthesis of cellulose nanocrystals using Acid hydrolysis process.

2.4 Characterization

2.4.1 Particle Size Analysis (PSA) & Zeta Potential

Particle size and distribution of particles was measured using Nano Particle size analyser (Model HOR1BA -52-100). The powdered NC was dispersed in water (RI 1.333) at 25^{o}C in a disposable cuvette and run for 60 seconds where particle size distribution graph was plotted. Value of zeta potential indicates the surface charge of nanoparticles, suggesting their electrophoretic mobility. The measures of dispersion stability were measured using the same instrument in which the zeta potential electrostatic forces were measured between -200mv to +200mv) at ambient temperature

2.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

To identify the functional groups, the FT-IR analysis was done for alkali treated, bleached, acid treated cellulose and nanocellulose using a Jasco FT-IR 6800 spectrometer (JASCO Japan) equipped with Attenuated Total Reflectant Unit (ATR) sensor. For this study, about 1.0 mg of sample was used and the spectra were taken with a spectral resolution of 4.0 cm^{-1} spanning the wave number range of 4000–400 cm^{-1}.

2.4.3 X-RAY Diffraction (XRD)

The XRD images was taken for Cellulose and Nanocellulose samples X- ray diffraction system (Model Ultima IV, RIGAKU, Japan). The analysis was performed on X- ray diffractometer operated at 40kV and 30mA, the pattern was recorded by Cu-Kα radiation with of 1.5401 Å. The sample of 0.5g was placed on glass substrate and it was mounted on sample stage and diffraction was measured.

2.4.4 Scanning Electron Microscopy (SEM)

The size and morphology of samples at different stages were investigated using a Quanta 250, FEI, Netherlands Scanning Electron Microscope. The samples were mounted on aluminium stubs with conductive carbon tape and sputtered with gold using a plasma sputtering apparatus under vacuum at 20mA for two minutes. The samples were then observed and imaged.

2.4.5 Transmission Electron Microscopy (TEM)

The size and internal structure samples at different stages were investigated using a FEI TECHNAI SPRIT Transmission Electron Microscope with 120 kV accelerating voltage. A drop of aqueous suspension was deposited on a copper grid (360 mesh) and allowed to dry under vacuum. The copper grid was then inserted into the instrument and images of the nanocellulose particles were captured under different magnifications.

3. RESULTS AND DISCUSSION

3.1 Particle Size Analysis

The graph showing the particle size and zeta potential is depicted in Fig.3. From the distribution graph, the size of the nanocellulose was found in the range of 213.5nm. Similar result was obtained by [3]. He reported that, the size of the nanocellulose was 178nm, however the size differs among different synthesis strategies for nanocellulose. As per the graph, the zeta potential for the synthesised NC as -34mV. [10] reported that the zeta potential of -48mV was obtained for nano cellulose and it indicates the stability of suspension in water solvent. The zeta potential of particles with more than ±30mV are normally considered as stable. So the obtained results indicates good stability of NC suspension. [11] reported the Zeta potential of -34.66mV, which is similar to obtaine results.

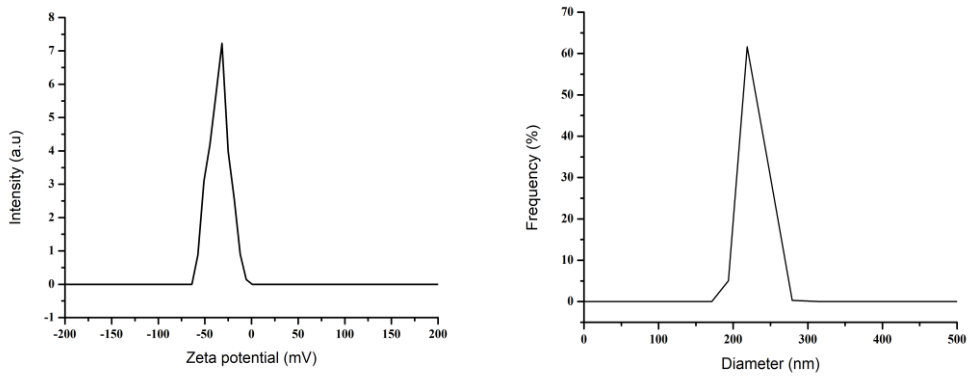


Fig.3. Particle size and zeta potential of nano cellulose

3.2 Fourier Transform Infrared Spectrometer (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) spectra of cellulose and nano cellulose provided information on functional groups present in the sample (Fig.4). FT-IR is a technique for identifying organic, inorganic, and polymeric materials by scanning them with infrared light. The results showed that an absorbance peak at 1217,1370, 1741 cm^{-1} for cellulose and the 1258, 1365, 1737cm^{-1} for nanocellulose was observed. Both cellulose and nanocellulose absorbance peaks at 1217 and 1216cm^{-1}show strong C-O stretching under the compound class alkyl aryl ether. The FTIR absorbance peak also shows strong S=O stretching at 1370cm^{-1}in cellulose and 1365cm^{-1} in nanocellulose under the compound class Sulfonamide and strong C=O stretching at 1741 cm^{-1} in cellulose and 1737 cm^{-1}in nanocellulose under the compound Aldehyde. Similar result was obtained by [12][13] reported that the absorbance peak at 1050 cm^{-1} is due to C-O Stretching, the peaks at 1730,1720 cm^{-1} are assigned to the C=O stretching indicates the microcrystalline cellulose. [14] also reports the C-O stretching to confirm the presence of cellulose.

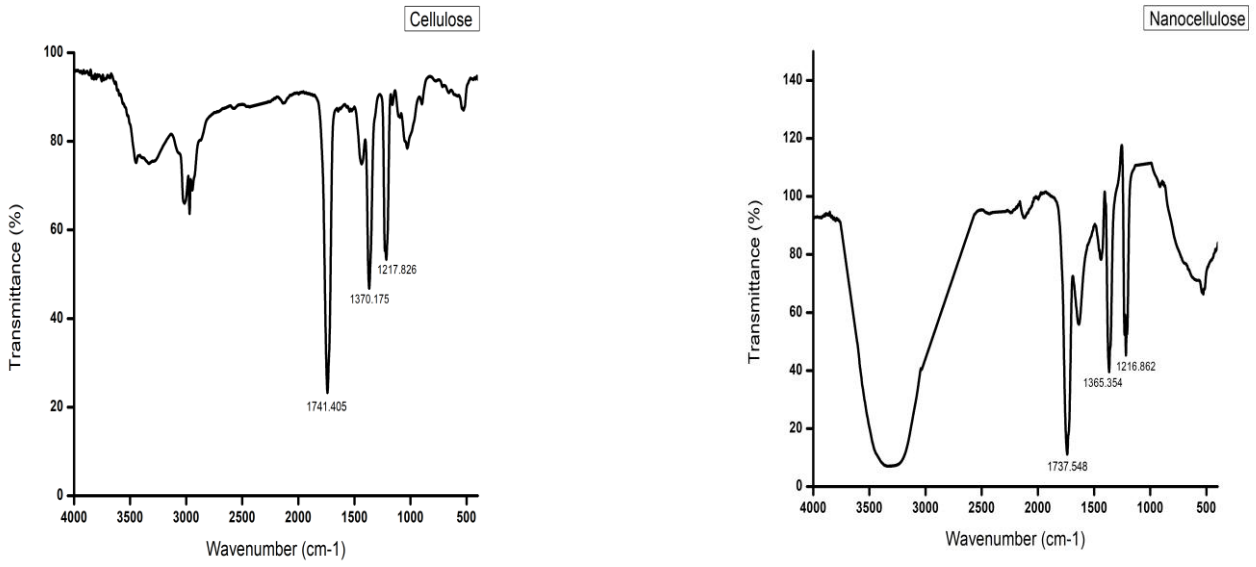


Fig.4. FTIR Spectra of cellulose and Nanocellulose

3.2.1 FTIR spectra at different stages of cellulose extraction

The fig. 5 depicts the FTIR spectra of extraction process of cellulose. The result showed that, the absorption band at 1744.35cm^{-1}showed the aromatic compound at C-H bending at weak appearance in all stages of hydrolysis process. The absorption band at 2969.33cm^{-1}showed medium appearance of C-H stretching under the compound Alkane.

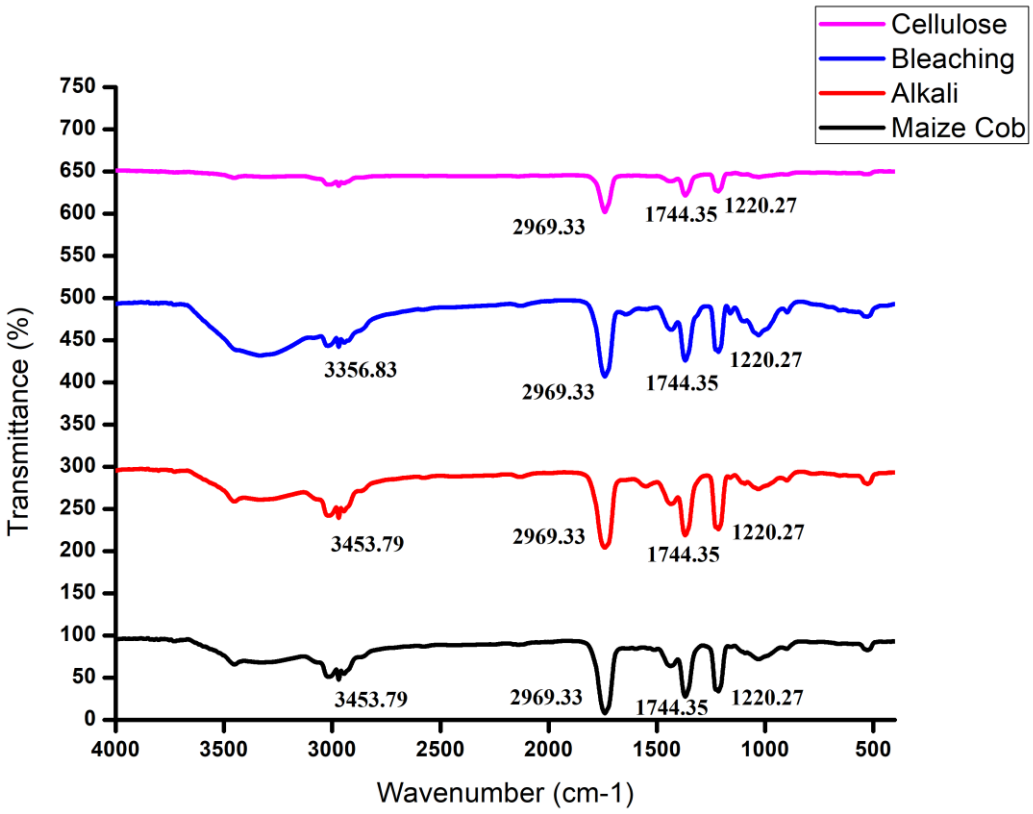


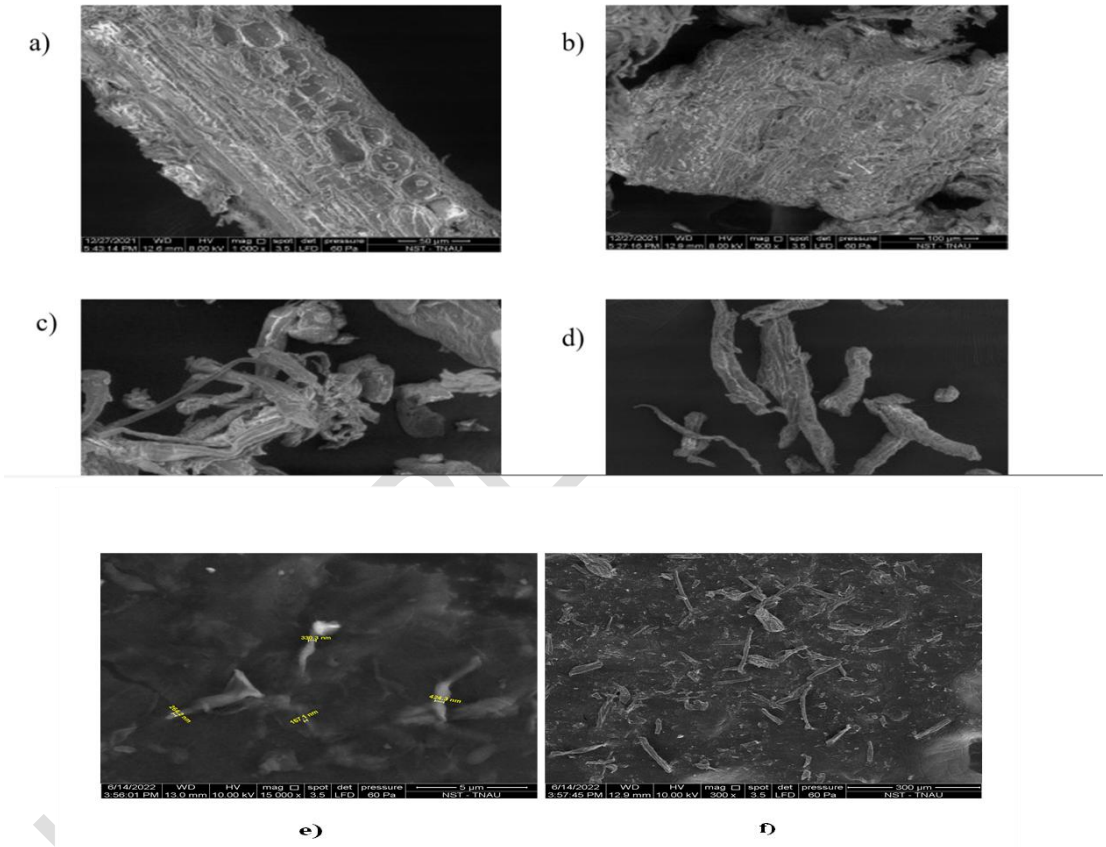
Fig. 5. FTIR spectra of different stages of cellulose extraction

The absorption band at 3453.79cm^{-1}showed strong broad appearance at O-H stretching under the compound Alcohol due to intermolecular bonding. [15] reported in their study about C-H bending, C-H stretching and O-H stretching at the wavenumbers of 1430 cm^{-1},2891cm^{-1}and 3461cm^{-1} respectively. The result indicated that the chemical composition of

microcrystalline cellulose was not altered during the nanocellulose extraction by alkaline treatment, acid hydrolysis, and nano milling. The gradual increase in a spectral band indicates the successful removal of lignin and hemicellulose during acid hydrolysis

3.3 SEM characterization

The SEM images of different stages of cellulose extraction are shown in Fig. 6. The image showed that, the corn cob image (a) shows a rough surface of different sizes and orientation of particles. This can be attributed to the fact that the corn cob powder contains all the components that give plant cell its rigidity and therefore rough appearance. After pre-treatment and subsequent hydrolysis increased homogeneity and lustre was observed (image e & f). Increased homogeneity and shine were found after pre-treatment and subsequent hydrolysis. These side effects are the result of the Maize cob's chemical treatment. Hemicelluloses, lignin, and pectins were successfully eliminated, resulting in the appearance of cellulose in the SEM image [16] . The image of a different extraction stages reveals a rough surface with particles of various sizes and orientations. The cluster of fibres diameter ranging from 160nm to 780nm. [17] reported that cluster of particles with varying diameters ranging from 24µm to 200µm was observed.

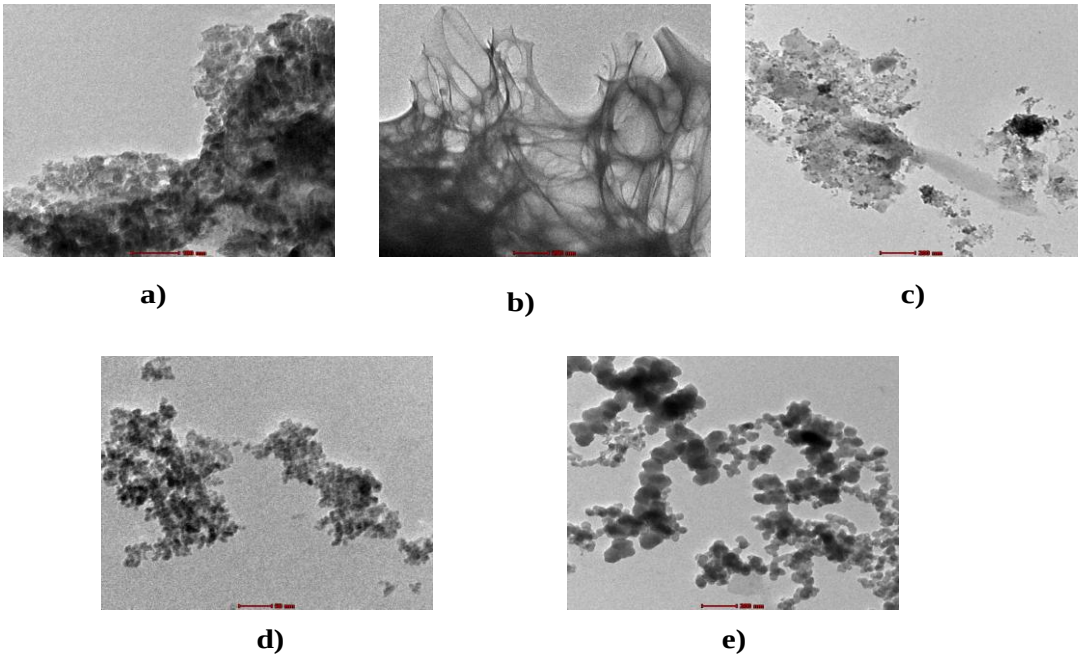


(a) Maize cob, b) Alkali Treatment, c) Bleaching, d) Cellulose, e,f) Nanocellulose

Fig.6. SEM images of different stages of cellulose extraction

3.4 TEM characterization

The ultra-structural morphology of sample at different stages was investigated using a Transmission Electron Microscope. the results are given in Fig. 7. The result clearly depicting the cluster of particles with fibre separation process to obtain cellulose. The bleached fibres had greater aggregation and inadequate defibrillation, according to the TEM analysis. The steam coupled chemical treatment improved the extraction of pure crystalline nano fibrils from Maize fiber, according to TEM measurement. The similar result was obtained by [17] and they reported that cluster of particles with varying diameters was observed



(a) Maize cob, b) Alkali Treatment, c) Bleaching, d) Cellulose, e) Nanocellulose

Fig.7. TEM images of different stages of cellulose extraction

3.5 XRD analysis

XRD pattern of Cellulose & Nanocellulose is shown in figure 8. The result showed that the diffraction pattern with wide peak around 2θ= 15.80, 22.03, 26.69, 40.44 and it showed the structure of cellulose [18] reported that, for nanocellulose, the XRD diffraction peak of around 2θ = 16.5°, 22.5° and 34.6° was obtained. The high intensity peak located at 22.79° for nanocellulose describes the crystalline nature of the material and the intensity value shows the amount of crystalline structure. There are two major peaks for all samples around 2θ of 15 degrees and 22 degrees. The characteristic peak at the 002 plane (2θ = 22º) is associated with crystallinity. The broadening of the peak is attributed to increased

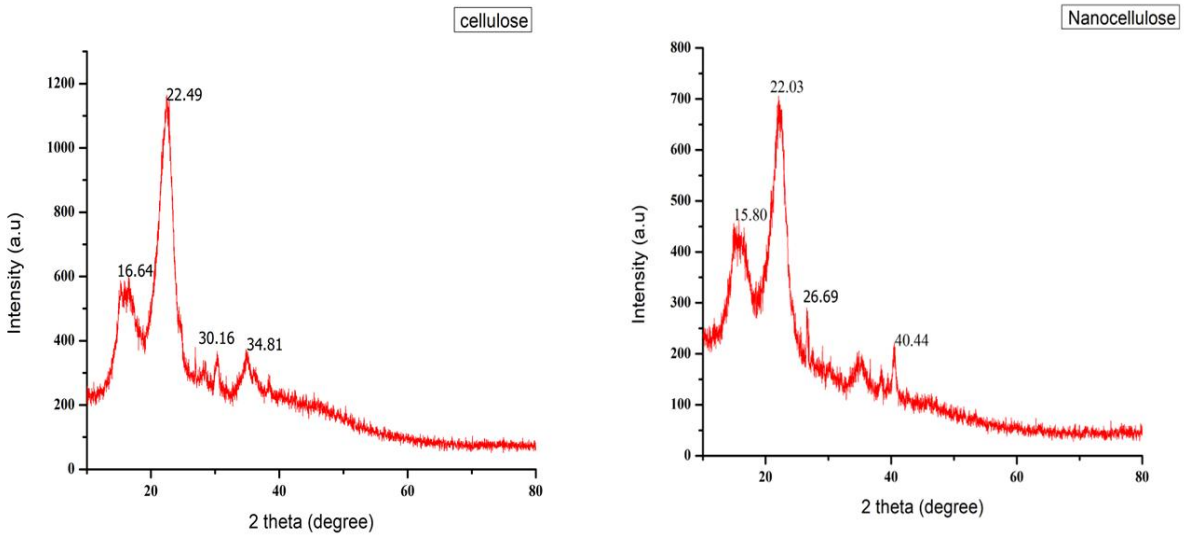


Fig 8. XRD Analysis of Cellulose and Nanocellulose

amorphousity as the corn cob contains all the amorphous cellulose. It is generally accepted that in the cellulose community that peak broadening is due to amorphous cellulose. H.A. Silvério *et al*. 2013 reported that the occurrence of peaks at 2θ = 15°,17°,21°,23° and 34° indicates a predominance of Nanocellulose. [19] reported the diffraction peaks were observed at 2 θ = 16°,22.5°and 34.5°, for extracted cellulose sample. [20] reported the crystallinity configuration of cellulose is shown by the peak at 2 values of 22.47°.

4. CONCLUSION

The acid hydrolysis procedure was used to extract nanocellulose from corn cobs. FT-IR, SEM, TEM, and PSA were used to characterize the extracted NC. The chemical treatment of the Maize cob improves the surface characteristics of the cellulose, which aids interaction between the cellulose and other molecules, according to the results. The obtained results confirm the Nanocellulose with the particle size of 213.5nm and zeta of -34.5mV and FTIR absorbance peak also shows strong S=O stretching at 1370cm^{-1}in cellulose and 1365cm^{-1} in nanocellulose and strong C=O stretching at 1741 cm^{-1} in cellulose and 1737 cm^{-1}in nanocellulose. Both cellulose and nanocellulose absorbance peaks at 1217 and 1216cm^{-1}show strong C-O stretching under the compound class alkyl aryl ether. The XRD analysis also shows peak around 2θ= 15.80, 22.03, 26.69, 40.44 shows the structure of cellulose. The SEM and TEM images clearly depicts the process of Acid Hydrolysis process, the fibre defibrillation and formation of cellulose and Nanocellulose. Nanocellulose-based paper appears to be the best packaging material because it provides adequate protection and packing for the product while also being ecologically friendly due to its renewable source and biodegradability. Nanocellulose is one of the most promising materials right now since it can be mass-produced and used in a wide range of applications.

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