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Refinement technique for nanocellulose extraction from corn cobs as a green material for environmental sustainability

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Abstract: Corn cob and other types of agricultural biomass waste are abundant and have several potential uses as renewable materials. A unique extraction approach for producing nanocellulose materials with precise control, scalability, and promising practical applications has been presented. Nanocrystalline cellulose was produced from corn cobs by mechanical treatment with ultrasonic technology, room temperature extraction for 30 minutes, and sulfuric acid concentrations ranging from 30 % to 60 % w/v. Nanocellulose has been effectively extracted from maize cobs with comparatively high yields and crystallinities ranging from 63.55 % to 71.76 %. The TEM data demonstrate the production of fiber nanoparticles with a size range of 15.3 nm to 2.1 nm. Simultaneously, SEM results match TEM findings. SEM pictures indicate smaller nanoparticles as sonication duration rises, but particle size does not vary with acid content. XRD analysis indicates an increase in the amount of crystalline cellulose in nanocellulose, demonstrating a notable transformation of cellulose. Nanocellulose and cellulose had similar FTIR spectra, distinct from the basic material of corn cobs. The FTIR analysis showed that the NaOH and subsequent bleaching treatments eliminated most hemicellulose and nearly all lignin throughout the conversion process. This work introduces a method for extracting nanocellulose from corncob waste utilizing standard ultrasonic technology under moderate conditions, at a cheap cost, in an ecologically responsible manner, with a high yield while maintaining its integrity.

Keywords: acid-hydrolysis; isolation; nano; sonication.

INTRODUCTION

Cellulose is the most abundant polymer in most plant biomasses.[1] Regardless, cellulose has numerous beneficial properties, such as being renewable, recyclable, eco-friendly, inexpensive, and possessing many mechanical powers.[2] Leftovers from plants like corn cobs, rice straw, etc., have been selected for manufacturing

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cellulose nanoparticles.[3] Nanocellulose (NC) is one of the most durable and rigid organic molecules. It has a very large surface area, is hydrophilic, and is adjustable to surface activation. Among the new materials to emerge this century, nanocelluloses (NC) and their derivatives have several promising uses in areas such as membrane technology, composites, healthcare, functional additives, water purification, and industrial implementations.[4-13] Pollution by chemical compounds is a global environmental concern based on the magnitude of the negative impact they have on the environment, plants, and human health.[14]

Corn cobs from corn production are non-edible agricultural residues that can be utilized to produce green fuel and chemicals. The demand for corn grain will increase as the population increases, resulting in the increase in corn cobs.[15]

Corn cobs are a rich source of cellulose with a range of 28 to 45 % and hemicellulose of about 38.78 %, but they also contain an adequate quantity of lignin (9.4 %).[12,16] Meanwhile, corn cob cellulose has a hydrophilic feature due to the presence of hydroxyl groups in each polymer module.[12] There may be advantages to the presence of lignin in lignocellulose nanofibrils—as residues in cellulose and nanocellulose packages—such as its potential antioxidant and UV absorption properties.[17]

This research seeks to highlight the novel approach employed in our previous study, which effectively minimizes the need for labor and financial resources, intending to utilize it for the extraction of nanocellulose from an alternative crop. Furthermore, we emphasize the significance of producing cellulose from agricultural byproducts, such as maize, to help preserve the environment.

EXPERIMENTAL

Samples and reagents

The plant material was sourced from Turkey and included cobs of *Zea mays* subsp. *Mays L*. The corncobs were initially washed with distilled water, followed by vacuum filtration to collect water. The samples were allowed to air dry at a temperature of 25 °C before being further dried at 100 °C using an oven with a suction system for 48 hours. Once pulverized, the substance was enclosed in a plastic container for preservation.

We obtained analytical-grade sulfuric acid, sodium hydroxide, and sodium hypochlorite from Sigma-Aldrich.

Preparations of Nanocellulose from Corn cobs.

Reducing acid concentrations, eliminating dialysis, and utilizing the freeze-drying process improve the hydrolysis method for NC preparations when compared to methods suggested by other researchers.[18] The dried corn cob powder was bleached at 80°C for 4 hours with 0.1 % sodium hypochlorite. The bleached fiber is washed and filtered with purified water before being dried. A bleached fiber of ten grams comes from the bleaching phase and remains hydrolyzed in 100 mL of sulfuric acid at numerous meditations (30 %, 40 %, 50 %, 60 %) using an energetic exciting. In order to terminate the reaction, deionized water was mixed with the solution of 100 mL, and the pH was adjusted to 7 through 1 % NaOH. A postponement is collected, filtered, and sonicated through ultra-sonication (UP400S) for different durations of

time (30, 60, 120) min. The NC fibers are then dried, converted to powder, and stored for future use.

Characterization of nanocellulose

In order to determine the characteristics of NC, the following equipment was utilized:

Transmission electron microscope (TEM).

A FEI technical G2 Split Biotic transmission electron microscope at 120 kV was used to examine the surface morphology required for the synthesis of nanofiber and nanoparticles prepared from corn cobs.

Field emission scanning electron microscope (FEI-SEM).

The morphologies and diameter of NC particles and fibers prepared from corn cobs were examined using FEI SEM (model Quanta 200FEG), configured to operate at (120 kV) at various magnification levels.

The X-Ray diffraction

X-ray diffraction was assessed using Micro Max 007HF DW. The diffracted power of the Cu Kα radiation (A = 0.154 nm, 45 kV, and 45 mA) was evaluated in the 2 fl range from 50 to 700; the maximum power was 1.2 kW.

Following equation (1),[18] the empirical crystallinity index (CrI) was determined. The formula for calculating the crystallinity index is as follows:

$$CrI = \frac{(I200 - Iam)}{I200} * 100\% \quad (1)$$

At a 2θ angle of approximately 22.5°, the greatest peak intensity is denoted by I200, whereas Iam represents the lowest diffraction at a 2θ angle of around 18°.

Fourier transform infrared (FTIR) spectroscopy

FTIR (models VERTEX 70 and Hyperion scan optical microscopes) was used to characterize the structure and functional groups that were present in all samples. FTIR spectra were generated from KBr pellets, which were made by mixing KBr powder and samples homogeneously in a ratio of 99:1 (w/w) by scanning within the range of 1400–400 cm^{-1}.

RESULTS AND DISCUSSION

TEM images

The sonication and hydrolysis treatment of H_2SO_4 prepared from corn cobs led to the production of nanocellulose as nanorod-like and spherical nanoparticles, which were specified by applying various morphological techniques for nanomaterials.

The TEM images showed a rod-like shape with an average diameter of 38.5–74 nm. However, very interesting nanoparticles with a diameter of 2–17 nm were indicated in Fig. 1 for a sample sonicated for 120 min and 30 % H_2SO_4. Increasing the concentration of acid to 40 % with an ultrasonic treatment of 120 min led to the production of nanoparticles with a non-uniform shape and a diameter of 11–70 nm. The result in Fig. 2 clarifies the aggregation of nanoparticles with an average diameter of 42.3 nm for 120 min of sonication and 50 % acid. Aspherical

nanoparticles with an average diameter of 25–40 nm was obtained for sonication for 120 min with 60 % acid (Fig. 3).

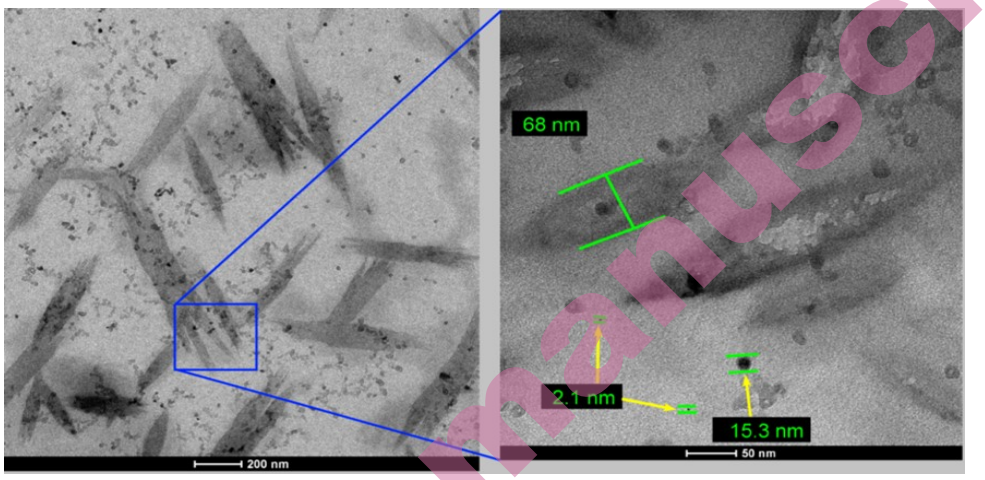

Fig. 1. TEM images of nanocellulose prepare by corn cobs sonicate for 120 min at 30 % acid.

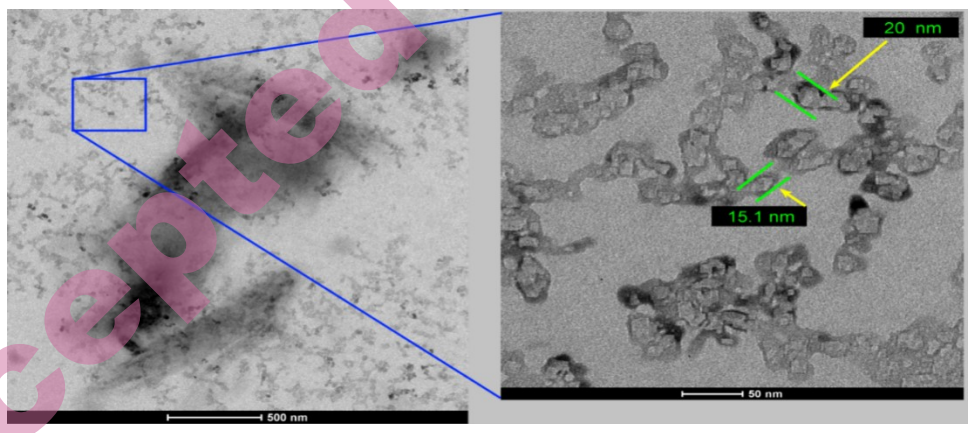

Fig. 2. TEM images of nanocellulose prepare by corn cobs sonicate for 120 min at 50 % acid.

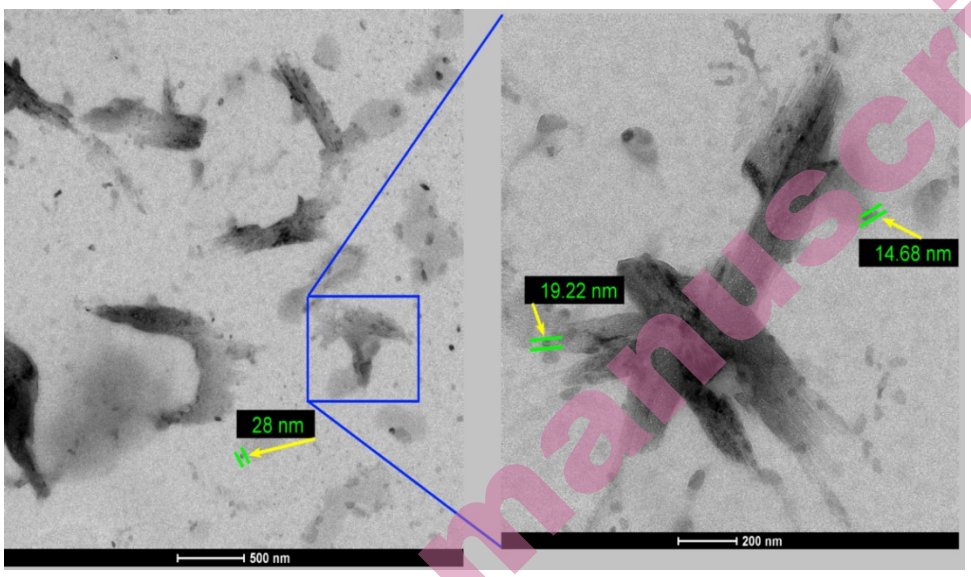

Fig. 3. TEM images of nanocellulose prepare by corn cobs sonicate for 120 min at 60 % acid.

After analyzing nanocellulose using transmission electron microscopy (TEM), it has been shown that the treatment, including 30 % H_2SO_4 for 120 min, is more favorable compared to other methods. This finding is distinct from previously published research. The research findings indicate that nanocellulose, ranging in size from 8.3 nm to 17 nm, was produced from rice husk.[19] On the other hand, a dendritic structure was formed from cotton, which was used as a plant source.[20]

SEM micrograph

SEM images of unsonicated samples of corn cobs were reviewed in Fig. 4. The surface of natural fibers demonstrates microscale fibers and microstructures. A sample sonicated for 30 min with 30 % acid comprises nanostructure fibers with an average diameter of 25 nm to 40 nm, accompanied by large amorphous regions. Increasing the sonication time to 60 min led to the detection of nano whiskers with an average diameter of 17–32 nm. The amorphous zones approximately vanished except for a few regions (Fig. 5). A sonicated sample for 120 min and 30 % acid proved long nano whiskers with an average diameter between 16 and 27 nm. These whiskers are separated into complex, smaller sub-whiskers. Amorphous regions disappeared completely, as illustrated in Fig. 6. The sonication process of 30 min with 40 % acid led to the incorporation of condensed and fine nano-web-like tiny fibers with an average diameter of 27 nm, as indicated in Fig. 7. When the sonication time increased to 60 min, it was observed that nanofiber structures originated with a 35 nm average diameter. With a sonication time of 120 min, it was verified that separated nanofibers arise with an average diameter of 38 nm.

With 30 min of sonication and 50 % acid, the nanostructures that appeared in the samples consisted of a nanonetwork with a 56 nm average diameter. While sonication time reached 60 min and 50 % acid, the results showed nanofibers with an average diameter of 42 nm.

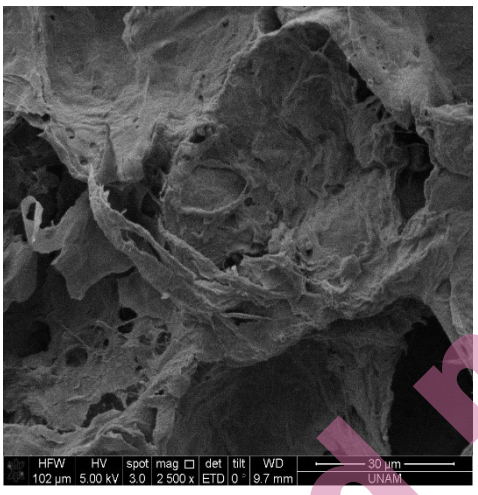

Fig. 4. SEM image for corn cobs.

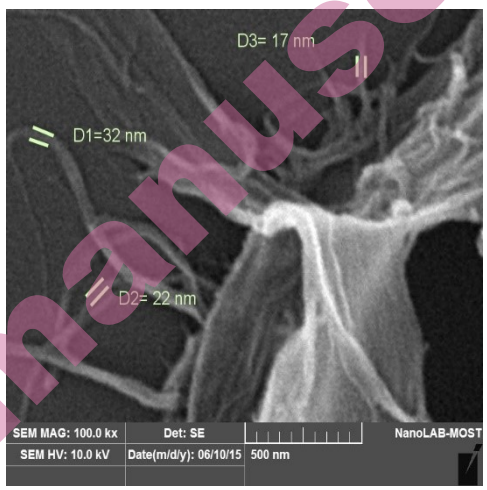

Fig. 5. SEM images of nanocellulose prepare by corn cobs sonicate for 60 min at 30 % acid.

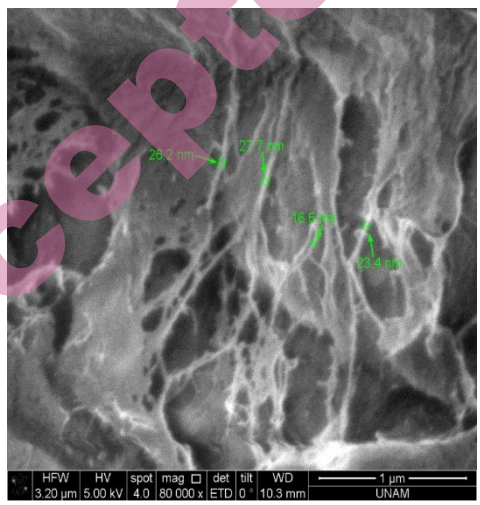

Fig. 6. SEM images of nanocellulose prepare by corn cobs sonicate for 120 min at 30 % acid.

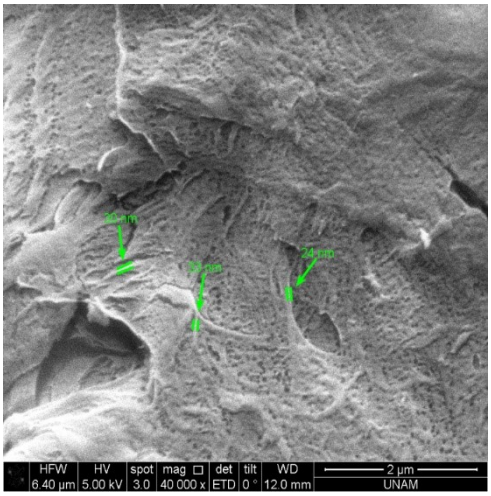

Fig. 7. SEM images of nanocellulose prepare by corn cobs sonicate for 30 min at 40 % acid.

It was indicated that branched nanofibers occurred at 120 min of sonication time and 50 % acid with an average diameter of 31 nm (Fig. 8). With 30 min of sonication time and 60 % acid, the results indicated a 34.5 nm average diameter. When the sonication time reached 60 min with 60 % acid, the results revealed nano whiskers with an average diameter of 32 nm. Finally, at 120 min of sonication time and 60 % acid, a network of nanofibers existed in the sample with 46 nm average diameters (Fig. 9). SEM findings reflected a disappearance of amorphous regions from nanocellulose patterns.

The SEM results reveal that the diameters of nanocellulose vary based on the plant source and extraction process. The diameters are generally lower when derived from corn cobs than when derived from cotton. [20,21]

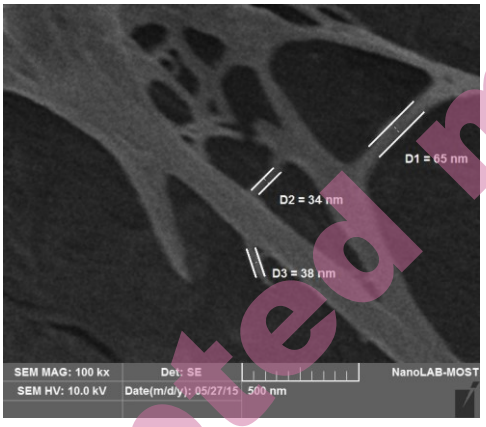

Fig. 8. SEM images of nanocellulose prepare by corn cobs sonicate 120 min at 50 % acid.

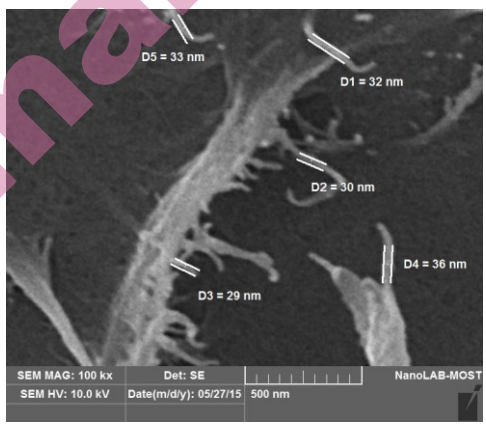

Fig. 9. SEM images of nanocellulose prepare by corn cobs sonicate 120 min at 60 % acid.

X-ray diffraction

To evaluate the crystallinity index and percentage of crystallin, the X-ray diffraction crystallinity index and the percentage of crystallin in untreated corn cobs and NC derived from corn cobs (Figs. 10 and 11). The NC specimens demonstrated three peaks at 29 = 18°, 22°, and 34°. The findings demonstrate that the percentage of crystalline material rose from 46.68 % in the untreated samples to 71.76 % when the amount of acid was injected and the duration of sonication was increased (Table 1). These findings exhibit a comparatively elevated level in comparison to the findings of other studies. [22]

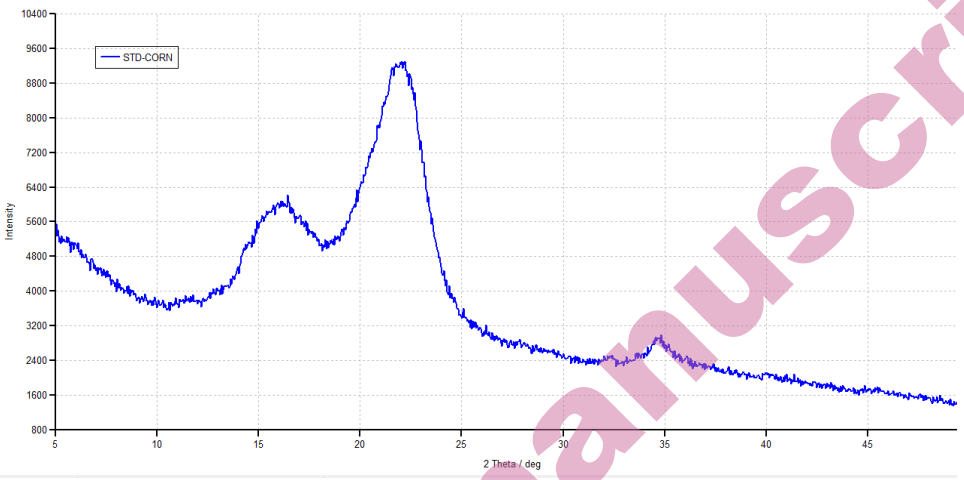

Fig. 10. X-ray diffraction pattern of untreated corn cobs.

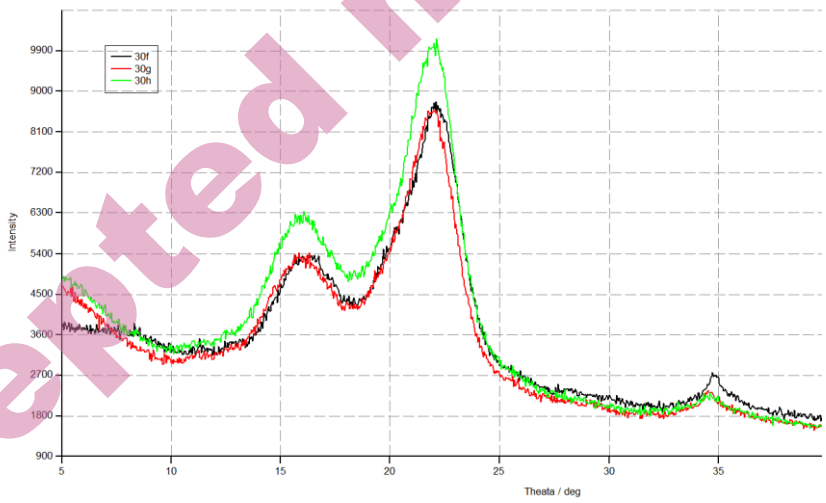

Fig. 11. X-ray diffraction patterns comparisons of nanocellulose prepared from corn cobs at different sonication time (30,60,120) min at 30 % acid.

The micro-jet produced by ultrasonic cavitation broke down the cellulose surfaces, and fibrillations were acquired; therefore, the surface expanse increased, accelerating the oxidization response[23] because of the mechanical potential required under ultrasonic strength for the insolvent to crystallize the configuration of the thin layer of cellulose tissue better than internal celluloses and reducing the crystallinity index. Furthermore, the confined tremendousness temperatures and compression circumstances (5000 K and 500 atm) with an aggressing shockwave established by cavitation may set up in the step downcast of the crystallized

arrangement of cellulose.[24] The deflection peak located at 20 = 22.5° for the sample that exhibited an advanced crystallinity index demonstrated that it remained strong and had enormous values compared to the peaks created by others. This nanocrystal forms the base of the nano whiskers web that increases the rheology and elasticity of nanocellulose. These interpretations point out preferable crystalline fields and are assured by the increase in the crystallinity index.[25]

Table 1. Crystallinity percentages and crystallinity indexes of nanocellulose at different acid concentrations and sonication times.

Treatments		crystallinity index	crystallinity %
Acid %	Sonication's (min)		
----	unsonicated sample	65.22	46.68
30	30	51.26	67.23
	60	51.44	67.31
	120	51.23	67.22
40	30	58.49	70.67
	60	54.55	68.75
	120	53.74	68.37
50	30	59.18	71.01
	60	60.64	71.76
	120	58.06	70.45
60	30	56.09	69.49
	60	50.37	66.83
	120	42.65	63.55

FTIR Determinations

FTIR spectroscopic analysis assessed the absorption frequencies to categorize the arranged NC. The robust comprehensive range from 3400 cm^{-1} to 3300 cm^{-1} is assigned to O-H extending,[26] while the peaks nearby are 2900 cm^{-1} allocated to C-H extending vibrations. This peak is reduced in concentration (Figs. 12 and 13) compared to that in non-sonicated raw substance varieties. The carbonyls assemble absorption peaks were noticed at 1650 cm^{-1}; at the same time, the peaks at 1730 cm^{-1} in the range referred to C=O extending of the acetyl chain with uranid esters series of hemicelluloses or to esters connection of carboxylic groups in lignans and hemicellulose.[27,28]

At the same time, the peaks of 1280 cm^{-1} belong to the C-O stretch of aryls set in lignan;[29] this peak completely vanished from the spectra of synthesized NC. This outcome proposed that all hemicelluloses and lignans be extracted from NC, particularly with the highest level of acid absorption and sonicate times. Additionally, the highest points at 1431 cm^{-1}, 1373 cm^{-1}, and 1317 cm^{-1} are correlated with the twisty vibration of the -CH_2, C-H, and C-O sets of the perfumed circle, respectively. This peak is seen in Fig. 13. The peak positioned at 1031 cm^{-1} to 1162.9 cm^{-1} qualified for the distortion of the C-H shocking vibrations and the

C-O-C pyranoses minimum circle.[30,31] Lastly, the peak of absorbances detected at 896 cm^{-1} is allocated to the identical C-O-C extending at (l-4)-glycosidic linkage that becomes less intense for NC varieties matched to the unsolicited samples.[32]

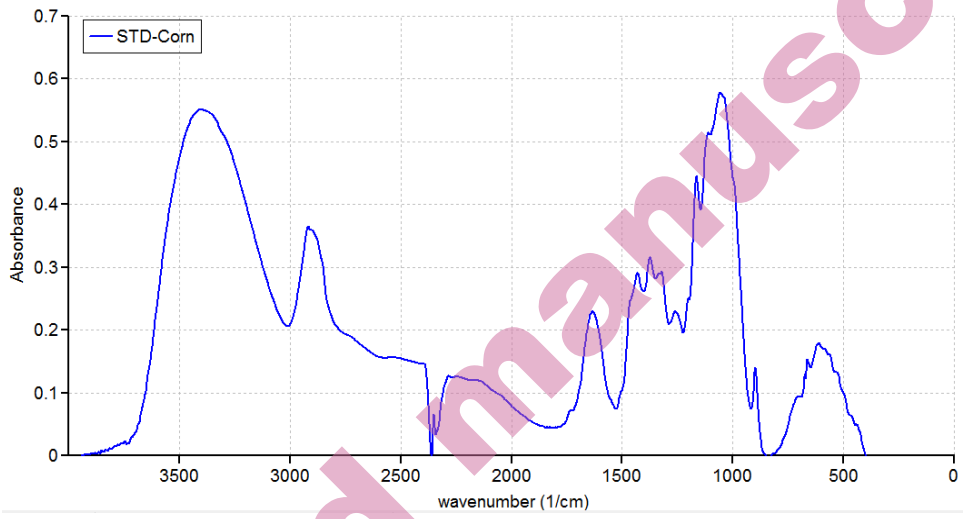

Fig. 12. FTIR Spectrum of corn cobs raw material.

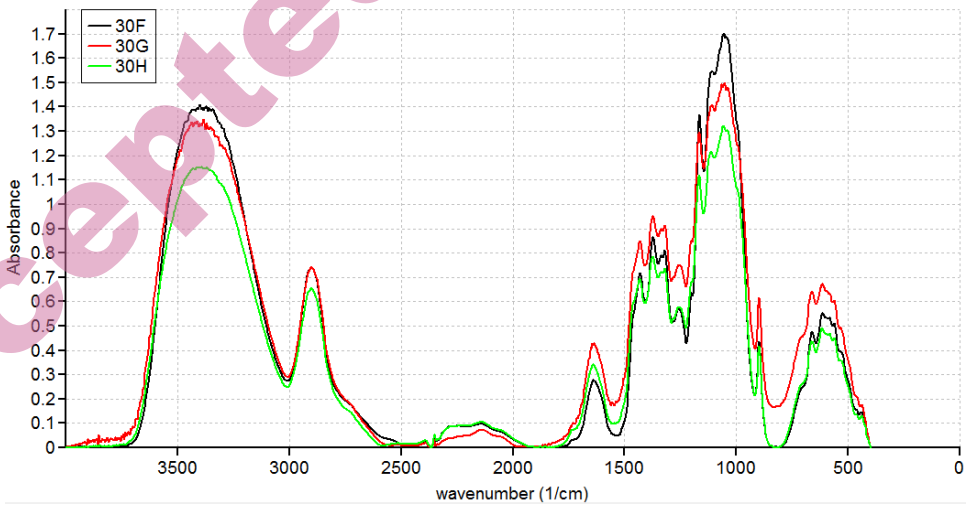

Fig. 13. FTIR variety patterns comparisons of nanocellulose prepared from corn cobs at different sonification time (30, 60,120) min at 30 % acid.

Following the completion of this procedure, both hemicellulose and lignin were eliminated, which supports the notion that the current approach is quite beneficial for the extraction of nanocellulose.

CONCLUSION

This paper has effectively demonstrated, for the first time, the use of the sonication technique coupled with the hydrolysis method in synthesizing cellulose nanoparticles. The results specify that the X-ray diffraction, TEM, SEM, and FTIR spectroscopy methods assure the formation of cellulose nanoparticles by this technology. Though the preferable outcomes under sonication's usage come from the remediation of 30 % acid sonicate for 120 min, these approaches designate that cellulose nanoparticles have a worthy prospect in the future for manufacturing purposes and corrective objectives. The FTIR analysis showed that the NaOH and subsequent bleaching treatments eliminated most hemicellulose and nearly all lignin throughout the conversion process. Though cellulose nanoparticles of honestly definite dimension result from this procedure, the precise cause of the modifications in the size of nanoparticles synthesized using corn cobs addressed under the two different conditions studied here (sonication time and acid concentration) must be further inspected.

И З В О Д

УНАПРЕЂЕНА ТЕХНИКА ЕКСТРАКЦИЈЕ НАНОЦЕЛУЛОЗЕ ИЗ КЛИПОВА КУКУРУЗА КАО ЗЕЛЕНОГ МАТЕРИЈАЛА ЗА ЕКОЛОШКУ ОДРЖИВОСТ

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Клипови кукуруза, као и друга отпадна пољопривредна биомаса су присутни у великој количини и имају значајну потенцијалну примену као обновљиви материјали. Представљен је јединствен приступ екстракцији за производњу наноцелулозних материјала са прецизном контролом, скалабилношћу и обећавајућим практичним применама. Нанокристална целулоза је добијена из клипа кукуруза методом која укључује механичку обраду ултразвучном технологијом и екстракцију на собној температури у трајању од 30 минута и при концентрацији сумпорне киселине у распону од 30 % до 60 % w/v. Наноцелулоза је ефикасно екстрахована из клипова кукуруза у релативно високим приносима и са степеном кристалиничности у распону од 63,55 % до 71,76 %. TEM подаци показују да се добијају наночестице у облику влакана, са распоном величина од 15,3 нм до 2,1 nm. SEM резултати одговарају TEM налазима. SEM слике указују да се мање наночестице добијају са повећањем трајања ултразвучне обраде, док величина честица не варира са променом садржаја киселине. XRD анализа указује на повећање количине кристалне целулозе у наноцелулози, показујући значајну трансформацију целулозе. Наноцелулоза и целулоза су имале сличне FTIR спектре, који су се разликовали од основног материјала из клипова кукуруза. FTIR анализа је показала да су NaOH и накнадни третмани бељења елиминисали већину хемицелулозе и скоро сав лигнин током процеса конверзије. Овај рад приказује методу екстракције наноцелулозе из отпадних клипова кукуруза, уз примену стандардне ултразвучне технологије под умереним условима, по јефтиној цени на еколошки одговоран начин, са високим приносом уз очување интегритета наноцелулозе.

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