

## A Novel Method for the Synthesis of Cellulose Nanofibril Whiskers from Banana Fibers and Characterization

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Alkali treatment coupled with high pressure defibrillation and acid treatment have been tried on banana fibers obtained from the pseudo stem of the banana plant *Musa sapientum*. The structure and morphology of the fibers have been found to be affected on the basis of the concentration of the alkali and acid and also on the pressure applied. Steam explosion in alkaline medium followed by acidic medium is found to be effective in the depolymerization and defibrillation of the fiber to produce banana nanowhiskers. The chemical constituents of raw and steam exploded fibers were analyzed according to the ASTM standards. Structural analysis of steam exploded fibers was carried out by FTIR and XRD. The fiber diameter and percentage crystallinity of the modified fibers were investigated using X-ray diffraction studies. Characterization of the fibers by SFM and TEM supports the evidence for the development of nanofibrils of banana fibers.

**KEYWORDS:** Steam explosion; nanofibrils; surface morphology; banana fiber

### INTRODUCTION

Cellulose nanofibers attain tremendous attraction due to their unique characteristics such as very large surface to volume ratio, high surface area, good mechanical properties including a high Young's modulus, high tensile strength (1) and a very low coefficient of thermal expansion (2), and formation of highly porous mesh as compared to other commercial fibers. These nanofibrous materials have recently attracted considerable interest in their role as reinforcing elements in nanocomposites. The goal of this study is to develop a commercial method for producing cellulose nanofibers by adopting the conventional steam explosion technique.

Steam explosion is one of the best ways of pretreating wood, which is to be subsequently used in chemical fractionation, biotechnological conversion, and the production of panels and composites (3–6). The steam explosion process was first introduced by Mason in 1927 to defibrate wood into fiber for board production (7). High pressure steaming followed by rapid decompression is called steam explosion. The steam explosion process includes saturating the dry material with steam at

elevated pressure and temperature followed by sudden release of pressure, during which the flash evaporation of water exerts a thermo mechanical force causing the material to rupture. The steam explosion process has been divided into two stages, namely, steam treatment at an elevated temperature and the subsequent explosive defibration. Morjanoff et al. (8) studied the two stages separately in order to quantify the relative benefits of each stage. Steam explosion results in the hydrolysis of hemicellulose within the fiber, and the resulting sugars can subsequently be washed out in water, leaving a residue of  $\alpha$ -cellulose and lignin (9). A substantial proportion of the hemicelluloses fraction is made water soluble, and the lignin fraction is modified. This results in a cellulosic substrate with improved enzymatic digestibility.

To reduce the content of noncellulosic compounds that cement the fiber aggregates, steam explosion can be used as a pretreatment. By this method, the fibers are liberated from the bundles as individual entities, and their efficiency as composite reinforcements should increase (10). Generally, the steam explosion process results in the hydrolysis of glycosidic bonds in hemicelluloses and, to a lesser extent, in cellulose. It also leads to a cleavage of hemicellulose–lignin bonds. The reactions result in an increased water solubilization of hemicelluloses and in an increased solubility of lignin in alkaline or organic solvents, leaving the cellulose as a solid residue with a reduced degree of polymerization

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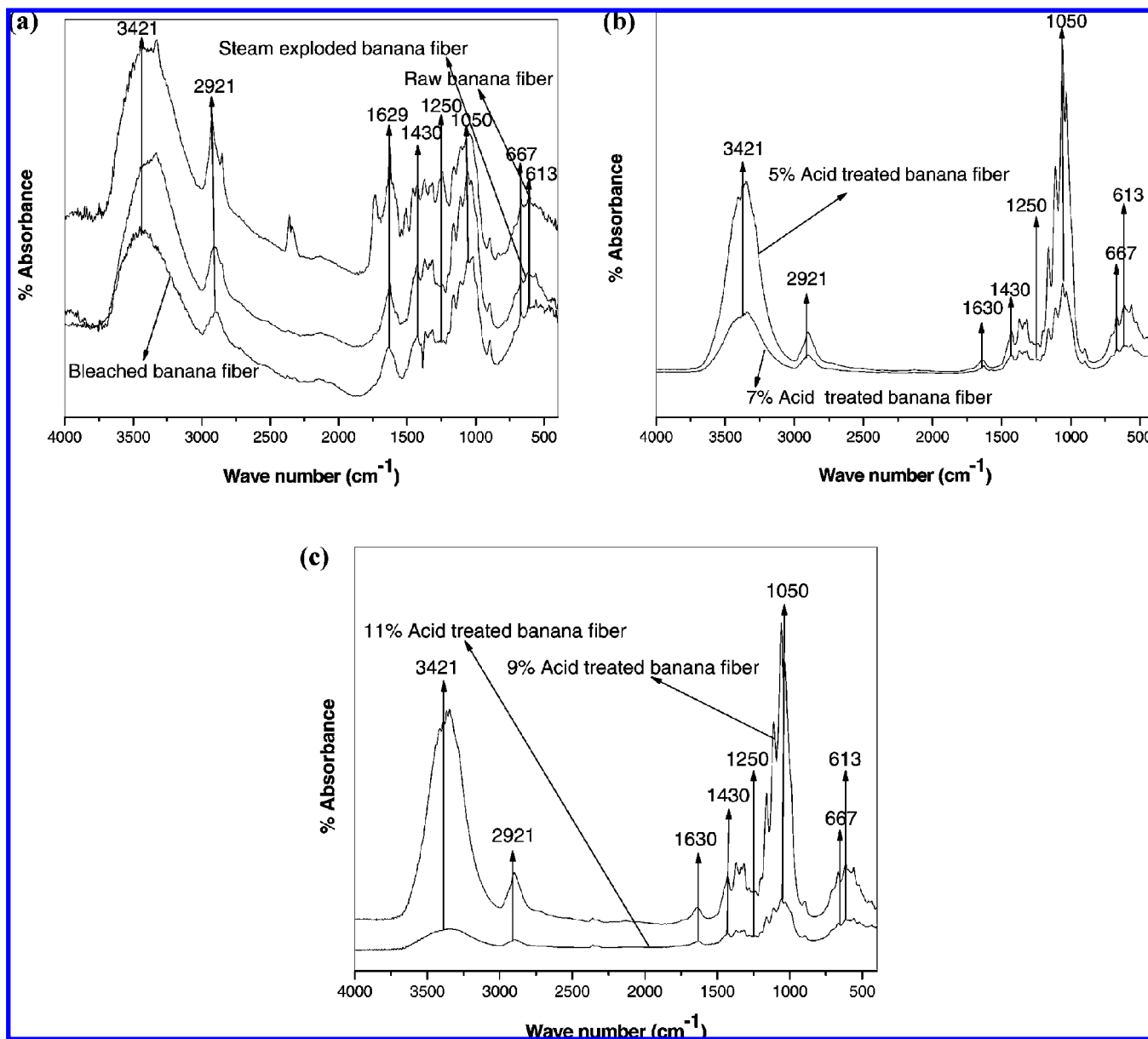
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**Table 1.** Chemical Composition of Untreated and Treated Banana Fibers

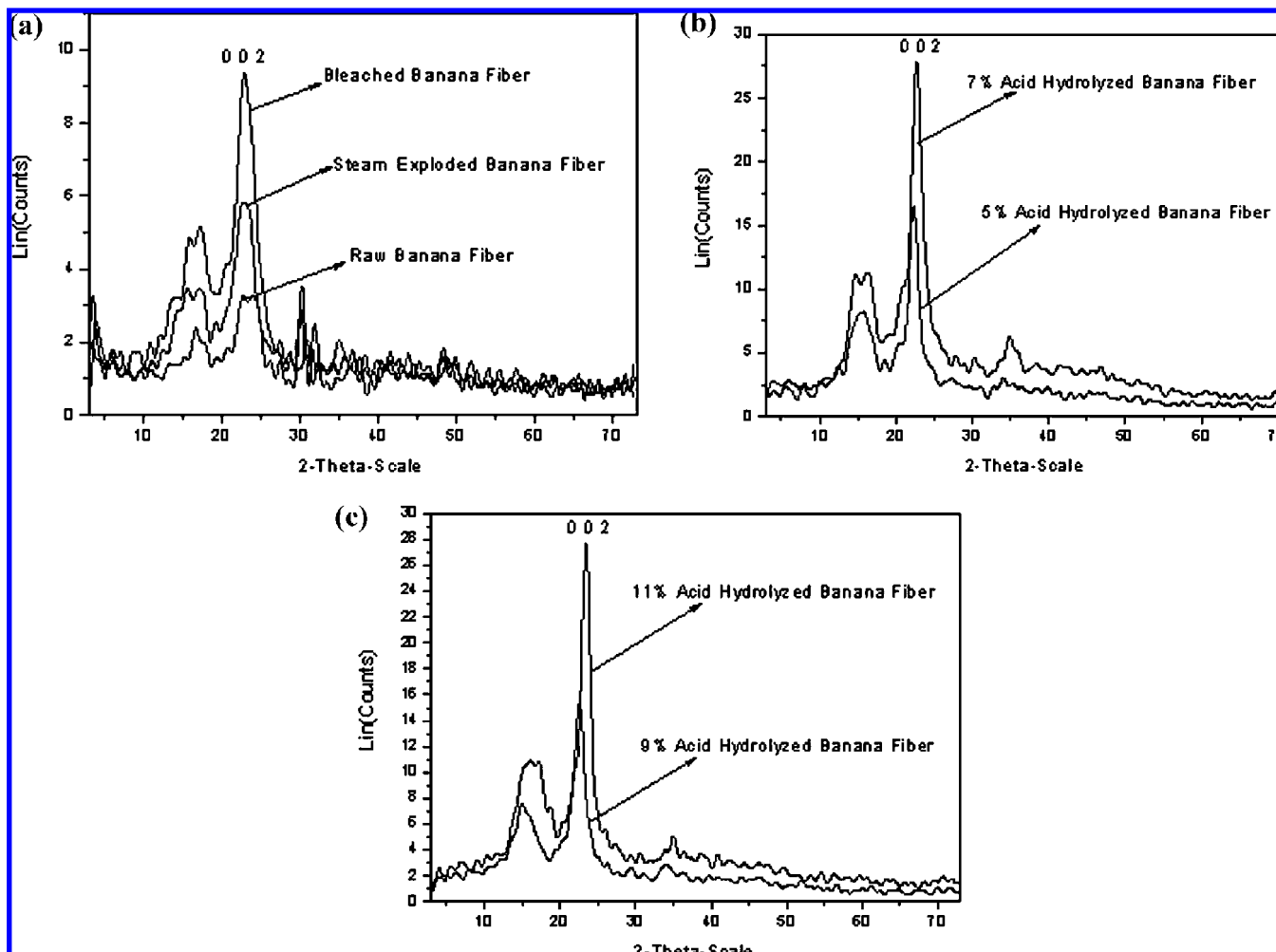
material	percentage of $\alpha$ -cellulose	percentage of hemicellulose	percentage of lignin	percentage of moisture content
raw fiber	64.04 $\pm$ 2.83 <sup>a</sup>	18.60 $\pm$ 1.62	4.90 $\pm$ 0.69	10.36 $\pm$ 0.47
steam exploded fiber	82.37 $\pm$ 2.52	13.97 $\pm$ 0.41	3.64 $\pm$ 0.53	10.48 $\pm$ 0.36
bleached fiber	95.86 $\pm$ 0.55	0.38 $\pm$ 0.02	1.86 $\pm$ 0.39	10.53 $\pm$ 0.42

<sup>a</sup> Mean  $\pm$  SD ( $n = 3$ ).**Figure 1.** (a) FTIR spectra of raw, steam exploded and bleached banana fibers. (b) FTIR spectra of steam exploded banana fibers in 5%, 7% acidic medium. (c) FTIR spectra of steam exploded banana fibers in 9%, 11% acidic medium.

(DP). Jiebing et al. states that from a chemistry point of view, the structural changes taking place in the steam explosion of biomass are similar to those occurring in steam treatment (11). The increased reactivity of steam exploded polymers results in derivatives with well defined and reproducible physical–chemical properties or selective degradation products that can be used to obtain advanced materials. The steam explosion treatment, which has been extensively studied as a promising pretreatment process by several authors, Tanahashi et al. (12, 13), Ruiz et al. (14), Yamashiki et al. (15), Excoffier et al. (16), Donaldson et al. (17), Kokta et al. (18), and Chornet and Overend (19), to increase accessibility and

separate the main components of lignocellulosic biomass (cellulose, hemicelluloses, pectins and lignin), could be an alternative to the conventional process of extracting the fibers from the plant. Recently, steam explosion has been considered an effective pretreatment (20) of waste cellulosic materials for further processing. The resultant material is finely divided, and the main components, cellulose, hemicelluloses, and lignin, are separated.

Steam explosion was originally applied in the separation of plant fibers and starch. Recently, this method has been used in the modification of cellulosic fibers such as cotton and flax (21). Three types of cellulose (softwood pulp, hardwood pulp, and



**Figure 2.** (a) XRD curves of raw, steam exploded and bleached banana fibers. (b) XRD curves of steam exploded banana fibers in 5% and 7% acidic media. (c) XRD curves of steam exploded banana fibers in 9% and 11% acidic media.

**Table 2.** Fiber Diameter of Variously Treated Banana Fibers

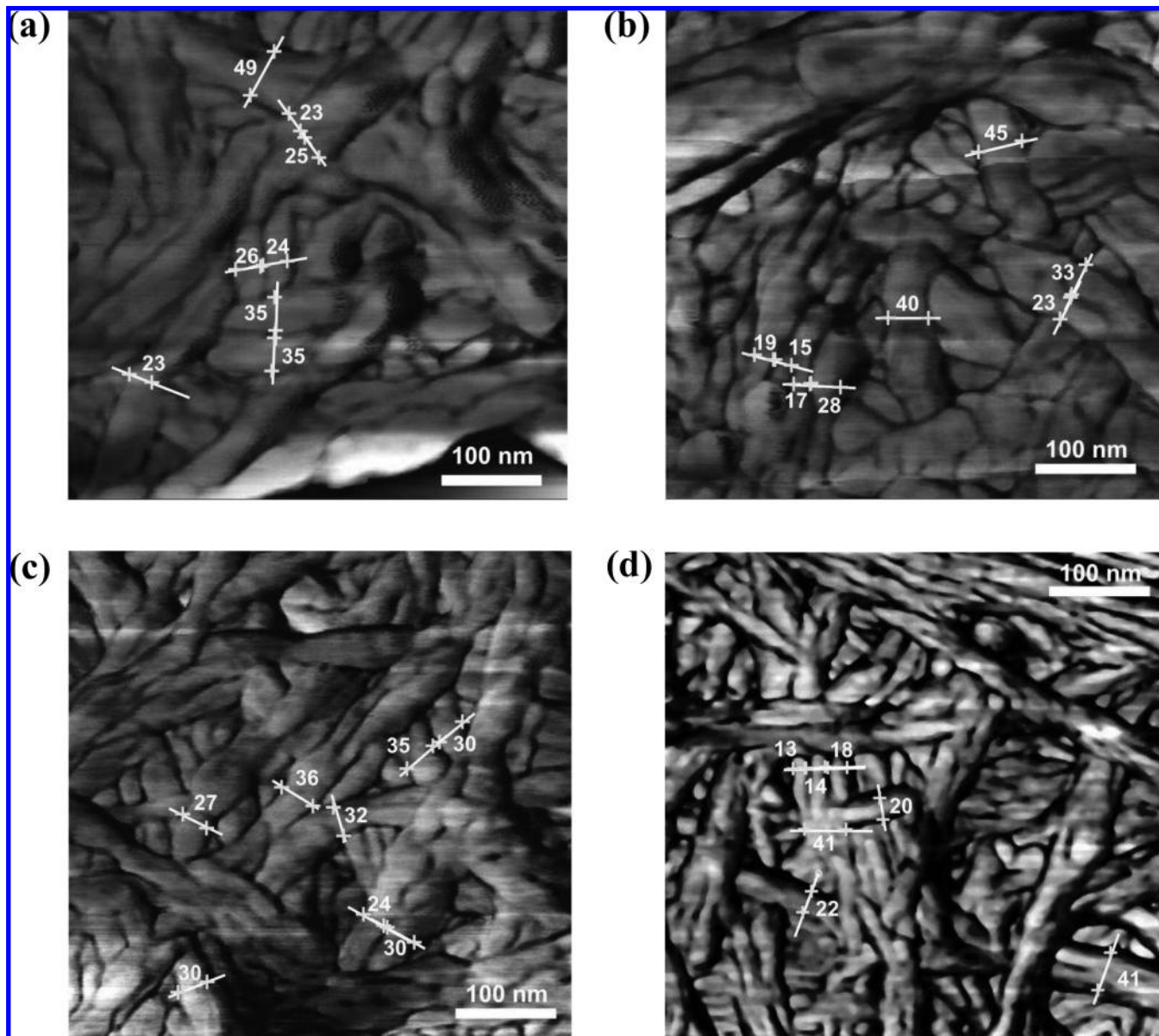
fiber stage	$\theta$ (Bragg angle)	$D$ (diameter of the fiber)	
		in nm	
5% oxalic acid treated, steam exploded, bleached banana fiber	11.16	8.49	
7% oxalic acid treated, steam exploded, bleached banana fiber	11.0845	7.11	
9% oxalic acid treated, steam exploded, bleached banana fiber	11.2795	6.24	
11% oxalic acid treated, steam exploded, bleached banana fiber	11.3415	5.13	

**Table 3.** Percentage Crystallinity of Raw and Variously Treated Banana Fibers

fiber stage	$I(0,0,2)$	$I_c$ (%)
raw banana fiber	$I(0,0,2) = I_{am} = 10.5$	
steam exploded banana fiber	16.4	35.97
steam exploded bleached banana fiber	22.9	54.18
5% oxalic acid treated, steam exploded, bleached banana fiber	32.4	67.59
7% oxalic acid treated, steam exploded, bleached banana fiber	34.8	69.83
9% oxalic acid treated, steam exploded, bleached banana fiber	38.3	72.58
11% oxalic acid treated, steam exploded, bleached banana fiber	39.8	73.62

cotton linters) were investigated by scanning electron microscopy, nuclear magnetic resonance, and mass spectrometry after the explosion (22). Steam explosion was also found to be effective for delignification of wood and cleaning of recovered cellulosic materials to produce the pulp for dissolving in *N*-methylmorpholine oxide (23). Focher et al. (24) reported that steam exploded pulps give sheets of higher density and improved breaking strength, burst, and tear indices. Steam explosion induces modifications in the primary structure of the hemicelluloses that are partly hydrolyzed and partly de-esterified, and to a better lignin softening, but above all to a modification of the tertiary structure of the cellulose that makes the fiber more

flexible and conformable, able to develop stronger interactions at the surface. Recently, the steam explosion treatment has been attractive for the degradation and separation of not only structural components, i.e., cellulose, hemicellulose, and lignin, but also antineoplastic constituents from plant biomass (25). The advantages of steam explosion include a significantly lower



**Figure 3.** (a) SFM of steam exploded banana fibers in 5% acidic medium. (b) SFM of steam exploded banana fibers in 7% acidic medium. (c) SFM of steam exploded banana fibers in 9% acidic medium. (d) SFM of steam exploded banana fibers in 11% acidic medium.

environmental impact, low energy consumption, lower capital investment, and less hazardous process chemicals. To date, steam explosion has been used mainly to modify the cellulosic materials. We have recently applied this technique to a bast fiber (e.g., banana fiber) to produce nanofibers for the first time.

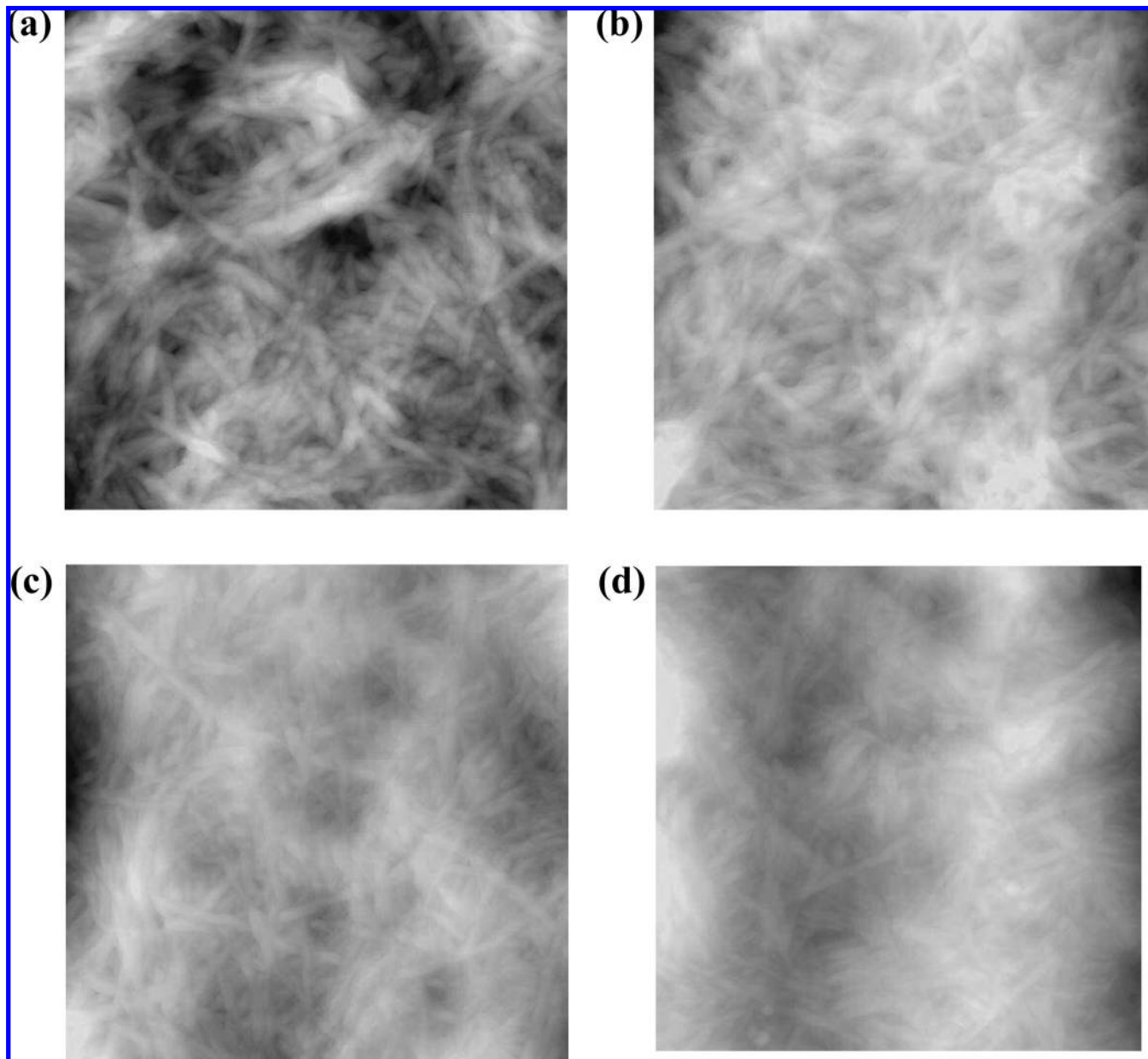
The method adopted includes alkaline steam treatment, bleaching, and acidic steam treatment phases. The immersion of lignocellulosic fibers in dilute alkaline medium facilitates the adhesive nature of the fiber surface by removing natural and artificial impurities, and causes the separation of structural linkages between lignin and carbohydrate and the disruption of lignin structure (26). The aim behind the bleaching process is the removal of lignin left after the alkaline steam treatment. The bleaching treatment done in the presence of sodium chlorite solution popularly used in laboratories to remove lignin from the vegetable fibers helps in the removal of phenolic compounds or molecules having chromophore groups in order to whiten the fibers (27). The mechanism of bleaching involves oxidation of lignin, which leads to lignin dissolution and its degradation. Further treatment (acid steam treatment), which helps in the produc-

tion of cellulose nanofibrils, is the main phase of the adopted method. Acid treatment hydrolyzed the traces of hemicelluloses and lignin remaining after the bleaching phase by breaking down the polysaccharides to simple sugars and hence released the cellulose fibers. The combined acid steam treatments effectively reduce the long micro fibril chains to nanodimensions by the maximum explosion of pressurized steam into the interfibrillar region.

In our present study, we have adopted steam treatment with subsequent explosive defibrillation. With this method, the substrate is loaded into a pressure vessel and heated by steam injection for a defined time–temperature period. At the end of this period of heat treatment, the pressure drop is suddenly made. A rapidly opening ball valve was used so that, after treatment, the contents of the reaction vessel were almost instantaneously depressurized and discharged through a nozzle.

Furthermore, banana fiber was used for the production of nanofibrils, which at present is a waste product of banana cultivation. In our earlier studies, banana fibers were found to be an effective reinforcement in a polymer matrix for





**Figure 4.** (a) Height SFM of steam exploded banana fibers in 5% acidic medium. (b) Height SFM of steam exploded banana fibers in 7% acidic medium. (c) Height SFM of steam exploded banana fibers in 9% acidic medium. (d) Height SFM of steam exploded banana fibers in 11% acidic medium.

making cost-effective composites (28–30). The present study was to apply the steam explosion process to banana fibers under various conditions to produce fibers in the nanometer range. We have employed the steam explosion technique in different media, followed by mechanical agitation to produce nanofibrils of banana fibers. These nanofibers were characterized by FTIR, XRD, SFM, and TEM techniques. The developed technique can be employed also for the preparation of nanofibrils of other natural fibers based on fruit, seed, and leaf. The novelty of the proposed technique is that we can produce nanofibrils by applying simple laboratory techniques.

#### EXPERIMENTAL PROCEDURES

**Materials.** The materials used for the study includes banana fibers (collected from Marthandom, Tamil Nadu, India), NaOH (commercial grade), acetic acid (commercial grade), sodium hypochlorite (commercial grade), oxalic acid (commercial grade), and a mechanical stirrer of type RQ-1.27 A and 8000 R.P.M.

**Preparation of Steam Exploded Banana Fibers.** Banana fibers were chopped into uniform size of approximately 10 cm. The fibers

were treated with 2% NaOH (fiber to liquor ratio 1:10) in an autoclave and kept under 20 lb pressure for a further period of 1 h. Pressure was released immediately. The fibers were removed from the autoclave, and the fibers were washed in water till they were rid of alkali. The washed fibers were allowed to drain off free flowing water.

**Preparation of Steam Exploded Bleached Banana Fibers.** The steam exploded fibers were bleached using a mixture of NaOH and acetic acid (27 and 78.8 g, respectively) and a mixture of 1:3 sodium hypochlorite solution. The bleaching was repeated six times. After bleaching, the fibers were thoroughly washed in distilled water and dried.

**Preparation of Steam Exploded Fibers in Acidic Medium.** The steam exploded bleached fibers were treated with oxalic acid of varying concentrations (5%, 7%, 9%, and 11%) in an autoclave till it attained a pressure of 20 lb. The pressure was released immediately. The autoclave was again set to reach a pressure of 20 lb, and the fibers were kept under that pressure for 15 min. The pressure was released and the process repeated 8 times. The fibers were taken out, washed till the washings no longer decolorized  $\text{KMnO}_4$  solution to make sure that the washings were free from acid.

**Mechanical Treatment of the Processed Banana Fibers.** The fibers were suspended in water and under continuous stirring with a mechanical stirrer of type RQ-1.27 A and 8000 R.P.M for 4 h. The suspension was kept in an oven at 90 °C till it was dry.

**Chemical Estimation.** Chemical compositions of fibers were estimated according to the following ASTM procedures:  $\alpha$ -cellulose (ASTM D1103–55T), lignin (ASTM D1106–56), holocellulose (ASTM D1104–56) and moisture content (ASTM D4442–92). The standard deviations were calculated by conducting three replicate measurements for each sample.

The  $\alpha$ -cellulose, hemicellulose, lignin and moisture content were calculated as follows:

$\alpha$ -cellulose percentage (A) =

$$(\text{Weight of the oven dry } \alpha\text{-cellulose residue}/W \times P) \times 100$$

Hemicellulose percentage =

$$[(\text{Weight of the oven dry holocellulose residue}/W \times P) \times 100] - A$$

Lignin percentage =

$$(\text{Weight of the oven dry lignin residue}/W \times P) \times 100$$

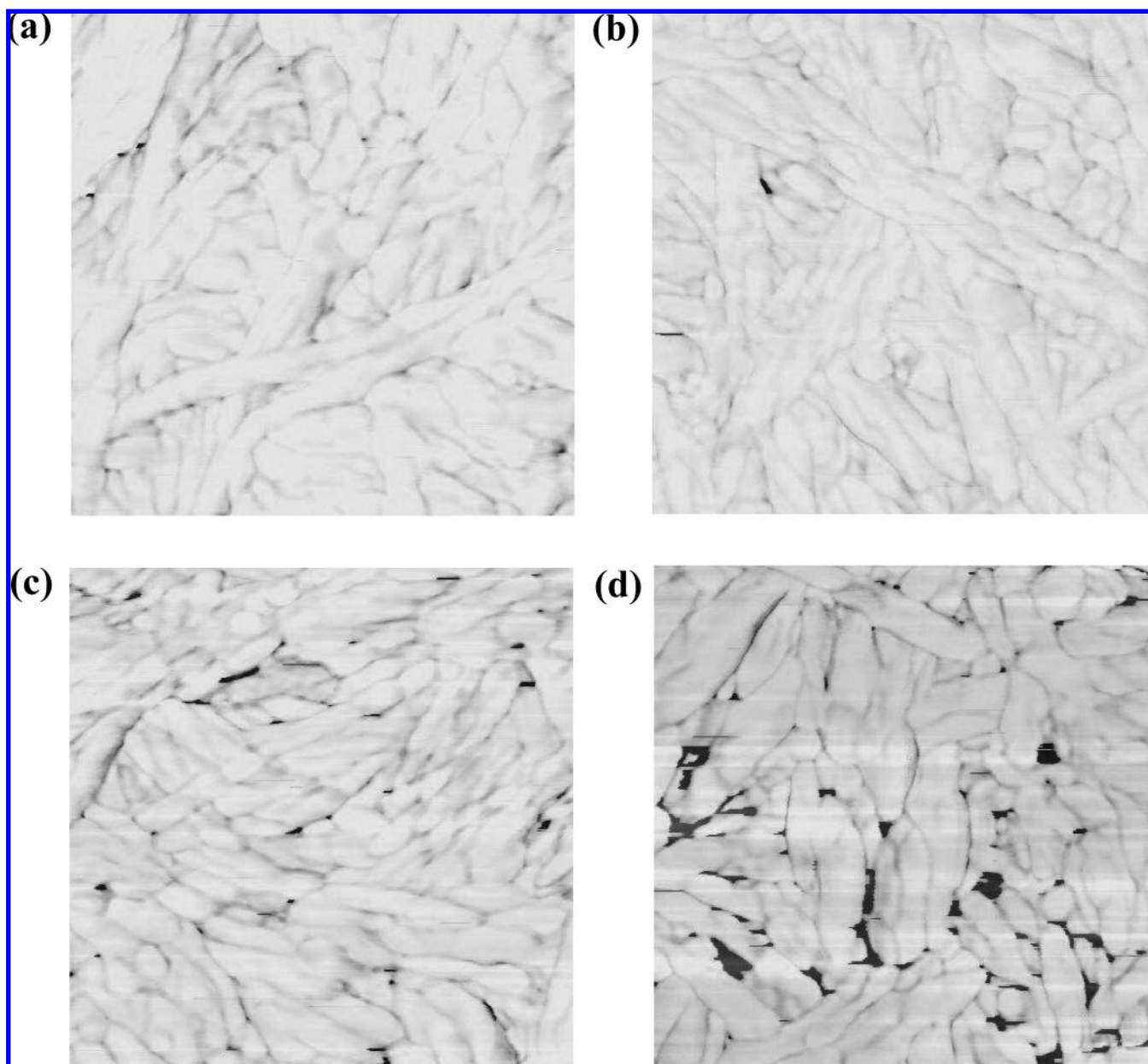
Percentage of moisture content =

$$[(\text{Initial weight of the fiber sample} - W)/W] \times P \times 100$$

where  $W$  is the weight of the original oven dry fiber sample, and  $P$  is the proportion of moisture-free content.

**Fourier Transform Infrared Spectroscopy (FTIR) Analysis.** Fourier transform infrared spectroscopy (FTIR) was used to identify the removal of various chemical constituents present in different purification levels by measuring the transmitted radiation of various infrared light wavelengths of different components. A Shimadzu IR-470 Infrared spectrophotometer was used to obtain spectra for the fibers after each chemical treatment. KBr disk method was followed in taking IR spectra. Fibers were ground and mixed with KBr (sample/KBr ratio, 1/99) to prepare pastilles. FTIR spectra were recorded in a spectral range of 4,000–400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  with a total of 20 scans for each sample.

**X-Ray Diffraction (XRD) Spectra.** In X-Ray diffraction technique (XRD), X-ray equatorial diffraction profiles were collected by a JEOL diffractometer, model JDX 8P, equipped with Cu  $K\alpha$  radiation ( $\lambda = 0.1541 \text{ nm}$ ) to investigate the relative crystallinity after the various stages of raw and treated banana fibers. The XRD spectra of the



**Figure 5.** (a) Phase SFM of steam exploded banana fibers in 5% acidic medium. (b) Phase SFM of steam exploded banana fibers in 7% acidic medium. (c) Phase SFM of steam exploded banana fibers in 9% acidic medium. (d) Phase SFM of steam exploded banana fibers in 11% acidic medium.

**Table 4.** Average Fiber Diameter of Steam Exploded Banana Fibers in Varying Acidic Medium Concentrations

acid concentration (%)	fiber diameter (nm)
5	27
7	25.5
9	19
11	15

nanofibers were obtained by air drying of the nanofiber suspension. The crystallinity determination was made using a powder X-ray diffraction method (PXRD).

**Scanning Force Microscopy (SFM).** The scanning probe microscopy images of the nanobanana fibers were made with a multimode SPM (Veeco Inc. Santa Barbara, USA) with a Nanoscope IV controller in tapping mode. For each sample, images were scanned on at least five different fibers. Usually, two different areas of each fiber were investigated. Only one representative image per sample is shown. For SFM analysis of cellulose, nanofibril samples for characterization were prepared by pipetting a 0.12 g/L aqueous whisker suspension, which was allowed to dry on a freshly cleaved mica surface. The sample was allowed to dry at room temperature overnight.

**Transmission Electron Microscopy (TEM).** Transmission electron micrographs of cellulose whiskers were taken with a Hitachi-600 transmission electron microscope with an acceleration voltage of 75 kV. Nanowhiskers were deposited from an aqueous dispersion on a microgrid covered with a thin carbon film ( $\approx 200$  nm). The deposited nanowhiskers were subsequently stained with a 2% uranyl acetate solution to enhance the microscopic resolution.

## RESULTS AND DISCUSSION

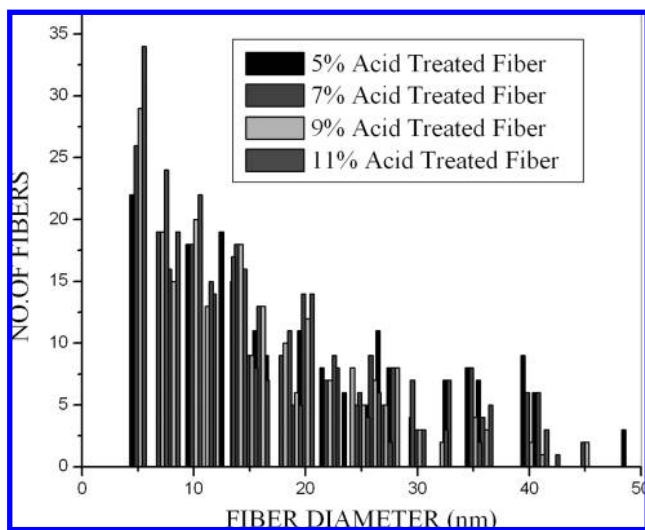
**Chemical Analysis of Raw, Steam Exploded and Bleached Fibers.** Table 1 shows the chemical composition of raw, alkaline steam exploded, and bleached fibers. It is clear from Table 1 that the raw fiber has the highest percentage of hemicellulose and lignin, and the lowest percentage of  $\alpha$ -cellulose. When the steam explosion process is done, we can observe that there is a decrease in the hemicellulose and lignin components present in the banana fiber. This shows that during steam explosion, substantial breakdown of the lignocellulosic structure, partial hydrolysis of the hemicellulosic fraction, and depolymerization of the lignin components have occurred, giving rise to sugars and phenolic compounds that are soluble in water as reported by other authors (31, 32). When the raw fiber is subjected to steam explosion in alkaline medium, the hemicel-

lulose and lignin components present in the raw fiber will dissolve out. Yamashiki et al. (33) proposed an explanation for the solubility of steam exploded cellulose in NaOH solutions, suggesting that during the steam explosion there is a partial breakdown of the intramolecular hydrogen bond at the C-3 and C-6 positions of the glucopyranose unit and that this results in significant variations in the network and strength of the hydrogen bonds of the cellulose hydroxyls. But the complete removal of these components does not take place. During the explosion, some changes occur in the arrangement of macromolecular chains. Slight rearrangement of macromolecular chains and the reduction of some polar groups make it more difficult for the fiber to absorb water and swell. Thus, the dissolving rate of the fiber slowed down. In addition, the explosion treatment might have removed some loose substances in the fiber surface leaving the hard structure, which is difficult to dissolve in the caustic solution (31).

During steam explosion, the hemicellulose is partially hydrolyzed and the lignin is depolymerized, giving rise to sugars and phenolic compounds that are soluble in water. The hydrolyses of glycosidic linkages in hemicellulose and the ether linkages in lignin are catalyzed by acetic acid formed at high temperature from acetyl groups present in hemicellulose (autohydrolysis). At the end of the process, the samples are explosively discharged, providing additional mechanical defibrillation. The cellulose is depolymerized and defibrillated (34, 35).

The percentage cellulose content of raw banana fiber increases when it undergoes steam explosion. When the steam exploded fibers undergo the bleaching process, we can see that there is further decrease in the percentage of hemicelluloses and lignin as well as an increase in the percentage of  $\alpha$ -cellulose component present in the fiber. The final fibers obtained after the bleaching process were found to have a high percentage (95.86%) of cellulose content. Therefore, the reinforcement ability of these fibers is expected to be much higher than that of other fibers that have less percentage of cellulose content. It is clear from the Table 1 that the treated fibers obtained after the bleaching process also have trace amounts of hemicelluloses and lignin components, which is also confirmed from the FTIR analysis of the banana fibers. As we go from raw fiber to the bleached fiber, we can see that there is a slight increase in the percentage of moisture content present in the fibers. Steam explosion resulting in higher availability of the hydroxyl groups distributed either on the surface of the cellulose crystals or in the nonordered regions. This is due to the increase in percentage of cellulose content during the process. Since, in pure cellulose, each unit has three free  $-OH$  groups, the moisture absorption rate increases with cellulose content. When the fibers were exposed to alkaline medium, swelling of the fibers as well as development of strongly hydrophilic ionic groups on the fiber surface were induced, which also promote the absorption of moisture.

**FTIR Studies.** Banana fibers in various forms were analyzed using FTIR to know about the various chemical constituents present in them. Figure 1a shows the FTIR spectrum of the raw, alkaline steam exploded, and bleached banana fibers. The peaks in the area of  $3421\text{ cm}^{-1}$  arise due to O-H stretching vibrations of hydrogen bonded hydroxyl (OH) group. The hydrophilic tendency of the natural banana fiber and steam exploded and bleached banana fibers are reflected in the broad absorption band in the  $3700\text{--}3100\text{ cm}^{-1}$  region, which is related to the  $-OH$  groups present in their main components. The peaks at  $2921\text{ cm}^{-1}$  are due to the aliphatic saturated C-H stretching vibration in cellulose and hemicellulose. The peak at  $1731\text{ cm}^{-1}$

**Figure 6.** Fiber diameter distribution curves of steam exploded banana fibers in 5%, 7%, 9%, and 11% acidic media.



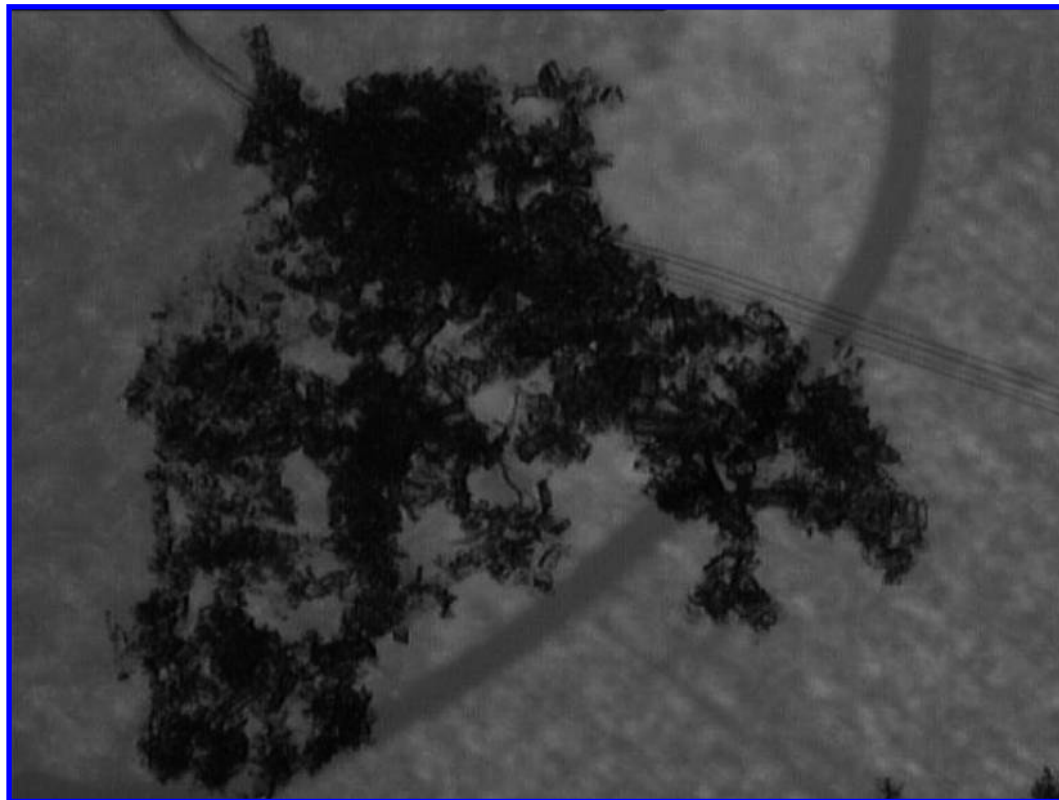


Figure 7. Optical microscopy of steam exploded banana fibers in acidic medium.

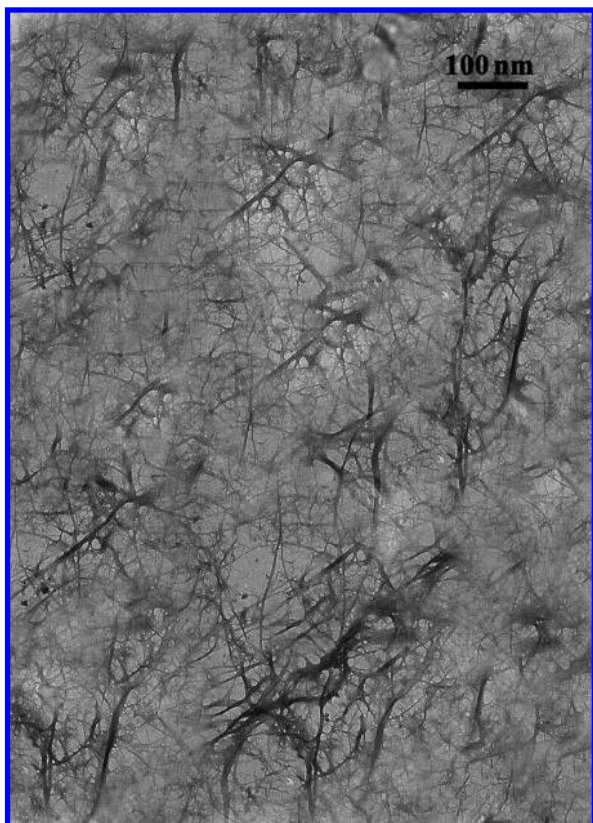


Figure 8. Transmission electron micrograph of steam exploded banana fibers in acidic medium.

in raw banana fiber is due to the acetyl and uronic ester groups of residual hemicelluloses or to the ester linkage of carboxylic group of the ferulic and *p*-coumaric acids of lignin (36). This peak is absent in the steam exploded and bleached banana fiber

due to the dissolution of the hemicellulose component present in the banana fiber during the process of steam explosion and bleaching. This peak may have also arisen because of the C=O stretching of methyl ester and carboxylic acid in pectin. In alkaline steam exploded and bleached banana fibers, this peak is absent, which may be due to the partial removal of carboxylic groups by alkali treatment through a process called de-esterification. During this process, the ester groups on the pectin were removed because of the ionization of pectin carboxylic groups (-COOH) and the formation of the corresponding sodium carboxylate (-COONa), which decreases the ability of hydrogen-type intermolecular bonds to form, and the solubility of pectins (37, 38).

Peaks at  $1629\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$  are indicative of the presence of lignin and attributed to the C=C vibration (39). The peak at  $1630\text{ cm}^{-1}$  is primarily due to the bending mode of the absorbed water with some contribution from carboxylate groups (36). The contribution from the absorbed water predominates in the case of bleached and acid treated fibers. The bands in the region  $1250\text{--}1056\text{ cm}^{-1}$  involve the C-O stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicellulose, lignin, and extractives (40). The peaks in the region  $1430\text{ cm}^{-1}$  are due to various lignin components (41). The intensity of the peak at  $1250\text{ cm}^{-1}$  is sharply weakened after bleaching treatment because of the removal of the hemicellulose material. The broad peaks at  $1050\text{ cm}^{-1}$  are assigned to ether linkage (C-O-C) from lignin or hemicellulose, while the peak at  $898\text{ cm}^{-1}$  is due to  $\beta$ -glycosidic linkages of glucose ring of cellulose (42). Peaks at  $667$  and  $613\text{ cm}^{-1}$  are due to the out-of-plane bending vibration of intermolecular H-bonded O-H group and out-of-plane O-H bending (41). The other peak at  $559\text{ cm}^{-1}$  is due to the torsional vibration of the pyranose ring (40). We can observe from Figure 1a that the bleached fibers also contain the characteristic peak due to lignin components in the region  $1430\text{ cm}^{-1}$  indicating



that the complete removal of lignin has not taken place. The peak area of the peaks due to the lignin components is found to be decreased from raw fiber to the bleached fibers. This proves that most of the lignin components were dissolved during steam explosion and on further bleaching process. In **Figure 1b** the peaks in the area of  $3421\text{ cm}^{-1}$  also arose due to O–H stretching vibrations of hydrogen bonded hydroxyl (OH) group. We can see that in steam explosion of the banana fibers in 5%, 7%, 9%, and 11% acid medium, the narrowing of this peak takes place because of the formation of free the –OH group by the breaking of H bonds. In **Figure 1b** and **c** the sharpening of the peak in the area  $2921\text{ cm}^{-1}$  takes place. This is due to the increase in the crystallinity in the fibers, showing the increase in the percentage cellulose components. The peak due to various lignin components in the region  $1430\text{ cm}^{-1}$  is also present in the steam exploded banana fibers in 5%, 7%, 9%, and 11% acid medium.

**X-ray Diffraction Studies.** XRD studies of the treated and untreated banana fibers were done to investigate the crystalline behavior and size of the fibers. From the XRD graphs, it is clear that the treated banana fibers show a crystalline nature. The fibers show increasing orientation along a particular axis as the fibers are treated under different processing conditions. **Figure 2a** shows the XRD pattern of untreated banana fiber. From the pattern, it is clear that the fiber is almost amorphous with very little crystallinity in it. **Figure 2a** also shows the XRD pattern of a steam exploded banana without bleaching, where slight crystallinity is evident at giving a relatively intense peak at  $2\theta = 22.6^\circ$ . The XRD pattern of steam exploded bleached fiber (**Figure 2a**), where the crystallinity is increased, gives a relatively intense peak at  $2\theta = 22.5^\circ$ . **Figure 2b** shows the XRD pattern of steam exploded banana fibers in 5% and 7% oxalic acid media, where crystallinity is evident at giving a relatively intense peaks at  $2\theta = 22.3^\circ$  and  $2\theta = 22.2^\circ$ , respectively. **Figure 2c** also shows the XRD pattern of steam exploded banana fibers in 9% and 11% oxalic acid media, also where crystallinity is evident at giving a relatively intense peaks  $2\theta = 22.6^\circ$  and  $2\theta = 22.7^\circ$ , respectively. The sharp peak in the X-ray diffraction pattern of the acid treated fibers exhibits a higher crystallinity due to the more efficient removal of noncellulosic polysaccharides and dissolution of amorphous zones. Accordingly, the above results demonstrate that hydrolysis took place preferentially in the amorphous region. This increase of crystallinity after acid treatment has been reported by several authors (43, 44). From **Figure 2a, b** and **c**, we can see that there is a broadening of the peak at maximum  $2\theta$ . This shows the evidence for the decrease in fiber diameter.

The fiber diameters ( $D$ ) of variously treated banana fibers are calculated using the Scherrer formula (45):

$$D = \frac{0.89\lambda}{B \cos \theta} \quad (1)$$

where  $K$  is a constant dependent on crystallite shape (0.89),  $\lambda$  = X-ray wavelength,  $B$  = fwhm (full width at half-max) or integral breadth, and  $\theta$  = Bragg angle.

**Table 2** shows the fiber diameter of different stages of banana fiber. From **Table 2**, it is clear that there is a decrease in fiber diameter as acid concentration is increased during steam explosion. Since raw and alkaline steam exploded fibers show amorphous nature, the Scherrer formula cannot be applied to these fibers. As we increase the strength of the acidic medium during steam explosion, we can see a decrease in fiber size and also the broadening of the peak at  $2\theta$ .

The crystallinity index ( $I_c$ ) was determined by using eq 2, where  $I(002)$  is the counter reading at peak intensity at a  $2\theta$

angle close to  $22^\circ$  representing crystalline material, and  $I_{am}$  is the counter reading at peak intensity at a  $2\theta$  angle close to  $22^\circ$  representing amorphous material in cellulosic fibers (46, 47).

$$I_c = \frac{I_c - I_{am}}{I_{(0,0,2)}} \cdot 100 \quad (2)$$

Steam explosion results in a cellulose with an increased degree of crystallinity and crystals of higher perfection and size, as shown by the width of the X-ray reflections before and after the steam explosion process (24). It is plausible that steam at high temperatures reorganizes the amorphous and paracrystalline cellulose regions releasing, from native cellulose, strains that arise during the crystallization phase of cellulose biosynthesis and the interaction of the cellulose with hemicellulose and lignin in cell wall formation.

**Table 3** shows the crystallinity of different fibers. We can see that as the concentration of the acidic medium during steam explosion increases, there is an increase in the percentage crystallinity in the banana fibers. This is due to the fact that during acid treatment the amorphous regions are readily attacked by dilute acid while the crystalline regions are more resistant to attack.

**Scanning Probe Microscopic (SPM) Analysis.** The SFM images of the variously modified banana fibers are given in **Figure 3a–d**. The results reveal that fiber diameter can be reduced to the nanometer range using repeated steam explosion in acidic medium. It was also observed that the fiber diameter depends on the concentration of the acidic medium used. **Figure 3a–d** reveal the change in the fiber diameter in the case of banana fibers when concentrations of the acidic medium during steam explosion were changed. Increase in the concentration of the acidic medium has been found to decrease the fiber diameter with fibers having a diameter less than 50 nm. This decrease in diameter of the fibers during acid treatment was also reported by other authors (44).

The SFM images are  $500 \times 500\text{ nm}^2$  and have a scale ranging from 0 to 40 nm for the height images and  $40^\circ$  for the phase images. A flattening procedure was applied to all SFM images. **Figure 4a–d** show the height SFM images of the variously modified banana fibers. From the SFM photographs, it is clear that the fibers are found to be agglomerated. **Figure 5a–d** show the phase SFM images of steam exploded banana fibers in 5%, 7%, 9%, and 11% acidic media, respectively. In these figures, the structures appear to be broader because of the folding with the SPM tip.

The phase SFM images show the reduction in fiber size as the concentration of the acidic medium is increased. It is also clear from the SFM images that as the concentration of the acidic medium is increased the agglomeration is also found to be increased. For steam exploded banana fibers in 11% acidic medium, we can see that the agglomeration is found to be increased, which is clear from the bulkiness of the fibers in the SFM image. The surface of the fibers is found to be smooth from the SFM images. One can see that as the acid concentration is found to be increased, there is an increase in the pits that appear on the surface of the fibers.

From the SFM photographs, the average fiber diameter is calculated using the computer program MATLAB. **Table 4** shows the average fiber diameter of the different acid hydrolyzed fibers. The fiber diameter distribution curves are shown in **Figure 6**. From the distribution curves, we can see that there is a decrease in fiber diameter as acid concentration is increased. As acid concentration is increased, the number of fibers with minimum fiber diameter is found to be increased, i.e., there is

a predominant increase in the number of fibers with minimum fiber diameter (i.e., 5 nm) in size for steam exploded banana fibers in 11% acid medium. The optical microscopical image of the steam exploded banana fibers in acidic medium is given in **Figure 7**. The figure shows the image in reflection with bright field illumination 40× of the fibers on the surface. The fibers were found to be agglomerated, and the shown region was covered with one of the smaller particles.

From **Table 4**, it is seen that as the acid concentration is increased there is decrease in the fiber diameter. The fiber diameter is the minimum for steam explosion of banana fibers done in 11% acidic medium (15 nm) and maximum for steam explosion of banana fibers done in 5% acidic medium (27 nm). Thus, using repeated steam explosion opens a new way of developing nanocellulosic fibers of natural origin.

**Transmission Electron Microscopy (TEM).** Transmission electron micrograph of steam exploded nanofibrils of banana fibers done in acidic medium are given in **Figure 8**. TEM analysis of the suspension revealed that nanofibrils have a needle-like structure. Uranyl acetate staining gave reasonable contrast between the fibrils and the carbon film. The presence of the heavy uranium in close vicinity of each whisker gave enough contrast for imaging. A tendency of agglomeration could be observed from TEM. It is not clear whether this was due to drying of the suspension onto the carbon film covering the copper grids or if it reflected the state of the suspension.

The average diameter and length were calculated from the electron micrographs using digital image analysis software. The average diameters of the nanofibrils were found to be between 4–5 nm, and the average lengths of the nanofibrils were found to be between 200–250 nm.

**Conclusions.** In summary, a novel method for the synthesis of nanofibrils of natural fibers was developed. Characterization of the synthesized nanofibrils was done by different modern techniques. The chemical composition of raw, steam exploded, and bleached banana fibers were determined. From the chemical examination, major constituents of these fibers were found to be cellulose. The percentage of cellulose components were found to be increased during steam explosion and the additional bleaching process. The lignin and hemicellulose components were found to be decreased from raw to the bleached fibers. The IR studies give evidence for the dissolution and chemical modification that occurred during steam explosion and further treatment of the fibers for steam explosion in acidic medium. XRD studies were done to investigate the fiber size and percentage crystallinity of the modified fibers. The XRD studies also revealed that there is a reduction in the size of fibers during steam explosion in alkaline medium and reduction in size to the nanometer range during repeated steam explosion in acidic medium. The percentage crystallinity of the fibers was also found to be increased from steam exploded fibers to repeated steam explosion in acidic conditions. The XRD studies also reveal that as the concentration of the acidic medium during steam explosion was increased there was an increase in the reduction of fiber diameter and an increase in the percentage crystallinity of the banana fibers. The SFM analysis also shows that there is reduction in the size of banana fibers to the nanometer range (below 40 nm). The TEM analysis also supports the evidence for the formation of nanofibrils of banana fibers by repeated steam explosion in acidic conditions. The average length and diameter of the developed nanofibrils were found to be between 200–250 nm and 4–5 nm, respectively. This high aspect ratio, when compared to that of other

polysaccharide nanofibrils, coupled with low cost widens the applicability of these newly developed nanofibrils.

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