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Cellulose Nanofiber Production from Banana Rachis

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Abstract:
Rachis of banana with a33,5±1,2% of cellulose and 15,6±1,1% of lignin was usedas raw material for obtaining cellulose nanofibers by combining chemical and mechanical rupture treatment. The nanocellulose obtained was characterized by infrared spectroscopy, thermal gravimetric analysis, scanning electronic microscopy and transmission electronic microscopy. It is concluded that the chemical treatment removed 51,99% of total lignin, and cellulose fibers with 20-50 µm of diameter were obtained.Besides, the nanofiber obtained after the mechanic rupture had a size of 10-15 nm and a crystallinity index of 64,32%.

Keywords: biomass, materials, nanocellulose, degradation.

1. INTRODUCTION

The environmental sustainability, industrial ecology and energy efficiency are important aspects in the development of material´s future generation, products and process. The biodegradable products and those based on biomas sutilization contribute to increase the value of agricultural waste, as well as in science and technology innovation. Cellulose nanomaterials (nanocellulose) are an example of these, since these materials are obtainable from plant´s waste. Generally, this waste is called lingo cellulosic waste, because it isformed of lignin and cellulose mostly. In a way, lignocellulosic wasteis considered, an inexhaustible raw material source for obtaining value-added products[1], [2]. Among other things, Costa Rica is well-known for its large banana production, this agricultural activity has been one of its main economic activities for years. During 2017, Costa Rica generated more than US $ 1 billion through banana exports and more than 100,000 jobs[3], [4]. Although, banana cultivation is important for the local economy, it brings with it a series of waste that needs to be managed. Around 3,560,000 tons per year of the stem, leaf, flower and banana crown remain on the field. The process of removing the banana from the rachis in the packaging process generates about 111 million rachis or banana stalk (pinzotes) per year, which is equivalent to 33,000 tons of dry rachis fiber annually. Most of it is cut and fixed in the field and becomes in compost [5], [6]. It is estimated that 15% of the rachis (5,000 tons of fiber peryear approximately) is processed in composting plants. Between 10% and 15% is used for the paper production, office accessories, souvenirs and similar products[7]. Therefore, an important part of the rachis is discarded on farms without any additional use. This discarded amount of rachis is a great source of raw material for the creation of processes and materials of the latest generation and of greater value-added due to its chemical composition, which is mainly cellulose with 35.3% m / m according to Florian et al. (2019). Cellulose is a linear homopolysaccharide of β-1,4-D-glucopyranose. The monomer has hydroxyl groups that areable to form hydrogen bonds that give cellulose different properties, among which (i) the multi-scale microfibrillar structure, (ii) the existence of amorphous regions versus crystalline regions and (iii) natural high cohesion evidenced by a glass transition temperature greater than the degradation temperature [9]. From the cellulose biopolymer, nanocellulose is obtained, which has attracted the attention of researchers, not only as a mean of using a remainder, but also for its properties and applications in various fields[10]. Several types of cellulose can be obtained on a nanometric scale, such as: 1) nanocrystalline cellulose (CNCs or NCCs), cellulose nanocylinders (CNWs) 2) cellulose nanofibrils (CNFs or NFC) and 3) bacterial cellulose (BC). Therefore, different materials are acquired with different crystallinity, chemical surface and mechanical properties that make them attractive for researching[11]. Among the processes for obtaining nanocellulose there are TEMPO oxidation (2,2,6,6-tetramethylpipelidine-1-oxylradical), enzymatic hydrolysis or mechanical methods that include high intensity ultrasonification, high-pressure homogenization or grinding [12]–[14]. Although, the most common process is hydrolysis, which can be acidic or alkaline. The non-cellulosic components and amorphous parts of the cellulose chainsare removed from the pulp [14]. A large number of works have been carried out through hydrolysis. Mandal and Chakrabarty (2014), performed the synthesis of cellulose nanofibrils from sugarcane bagasse. Habibi (2014) managed to synthesize cellulose nanofibrils with a dimension of 10-30 nm and hundreds of nanometers in length. Furthermore, by mixing HCl and HNO_3, cellulose nanocrystals with excellent water dispersion are obtained[17]. The aim of this research is to find out the proper conditions for the nanocellulose production from banana rachis, and the use of chemical substances which are also environmentally friendly, andthese conditions must be scalable.

2. METHODOGY

2.1. Preparation of nanocellulose

2.1.1. Degradation of raw material

The nanofibrils collection beganwith the raw material degradation. Banana rachis were supplied by Chiquita Brands International Costa Rica. These rach is were dried and cut toapproximately 10 mm size, NaOH 2% solution was added in the relation of 1 g / 50 mL solution and it was processed at 121 °C and 15 lb pressure for 30 min. It wastaken out and washed until neutral pHwas achieved. The solution was decanted and washed for 10 min twice. The resultant mass was processed

again at 121 °C and 15 lb pressure for 30 min using acetic acid 6% for greater crystalline. It was taken out and washed until neutral pHwas achieved. The solution was decanted and washed for 10 min with $NaClO_2$twice.

2.1.2. NANOFIBRILS SYNTHESIS

The dilute cellulose was collected in the high potency sonifer Branson UltrasonicsTM SFX150. 60% amplitude was used during 30 min in a water bath to prevent warming. After that, nanocellulose was centrifuged and saved at 4-6°C temperature.

2.2. Characterization

2.2.1. Chemical characterization

The chemical composition of the banana rachis was determined according to the methods reported by the Technical Association of Pulp and Paper Industry (TAPPI). The extractives, lignin, holocellulose, hemicellulose, cellulose and ashes were identified. Those compounds were accessed according TAPPI standard T 207 cm-99, T 413 om-02, T 222 om-02, T 280 pm-99 and T 203 cm-99 respectively.

2.2.2 ***Microscopy and spectroscopy characterization***

2.2.2.1. Fourier transform infrared (FTIR) spectroscopy: To obtain the bands of the functional groups associated with the fiber components, also the absence and presence of lignin, a Fourier transform infrared spectra was recorded using aPerkin-ElmerFrontier FT-IR-ATR spectrophotometer. One scan as a sample was performed of 4000 cm-1 to 450 cm-1 without atmosphere suppression.

2.2.2.2. Thermogravimetric analysis (TGA): The residual lignin, specific degradation and quantity of each compound by means of the area under the curve were determined by Thermogravimetric analysis. This analysis was performed using TGA TA-Instrument Q5000 analyzer, while an inert atmosphere was used and a heating rate of 5 ◦C/min from 25°C to 600°C.

2.2.2.3. Confocal laser scanning microscopy (CLSM): the residual lignin and the cellulose in each fiber was monitored by CLSM Olympus FV1000 Flu view IX81. It was adapted with three lasers: Multi Ar (458, 488, 515 nm), HeNeR laser (633 nm) and HeNeGlaser (543 nm); and a fluorescence unit. The presence of cellulose was evaluated using 0.01% M2R calcofluor dye for 5 min and subsequently dried at room temperature. The fiber was observed with CLSM at 405 nm of wavelength. Lignin was monitored by auto fluorescence at 488 nm wavelength.

2.2.2.4. X-ray diffraction (XRD): X-ray diffraction was used to determine the samples crystallinity and in relation with treatments performed. The XDR was carried out in a PAN alytical-Empyrean diffract meter with a 2θ angle ranging from 5° to 60°.

2.2.2.5. Scanning electronic microscopy: Electronic micro scopy HITACHI 3700-N was used to determine the morphologic changes in fiber by micrographics according to each treatment. Entropy changes were measured by image analyzation using ImageJ and the pluging GLCM texture.

2.2.2.6. Transmission electronic microscopy: Electronic micros copy HITACHI HT-7700 was used to determinate the size of nanocellulose fiber.

3. RESULTS AND DISCUSSION

3.1. *Chemical characterization*

The characterization rachis were determined according to the methods reported by the Technical Association of Pulp and Paper Industry (TAPPI). Data is presented in Table 1.

Table.1. Banana rachis chemical compositionaccording TAPPI standards

Compound	Percentage (%)
Cellulose	33,5±1,2
Water solubility	28,77±0,28
Ashes	25,85±0,55
Lignin	15,6±1,1
Hemicellulose	7,8±1,5
Extractives	2,97±0,27

Cellulose found in the banana rachis is relatively higher comparedwith other waste materials. Materials like wood exceeds 20% [18], [19], wheat straw and barley straw´s cellulose content is 30% and 33% respectively, banana rachis also contained more cellulose than nut shells, because these contained only 25%[20]. On the other hand, the lignin in the rachis is low, the light conditionsfor material hydrolysis are favored and finally cellulose is obtained. To remove lignin between and covering the fibers, high temperature or strong acids / bases solution according to hydrolysis is needed[21]–[24]. It is important to mention that holocellulose in rachis exceeds 40%, holocellulose constitutes an abundant sugar source, which makes the material important in subsequent hydrolysis [18]. Refferingto Table 1, as has been previously reported there was an extractives content of 9% (in water and ethanol), a cellulose content of 35,3% and hemicellulose content of 17,9%; also 6% of acid soluble lignin for the same variety of banana cultivated in Costa Rica (Musa Cavendish) [8]. Another authors have found cellulose content in different waste products of the banana plant,for example, a cellulose content of 37,3% in leaf sheaths or only 15,7% in floral stalk was found, while the lignin content varies on each part of the plant, rachis excel with a 10,5% which shows that values obtained in Table 1 coincide with the literature [25].

3.2. *Fourier transform infrared (FTIR) spectroscopy*

The spectroscopy is a complementing technique used for the interpretation of molecular structures. This technique is based on molecules vibrational modes, thus the functional groups related with macroscopy characteristics of materials can be identified[26], [27]. Figure 1 shows the infrared spectra obtained for banana rachis. It is observed that the band at 3340 cm^{-1} corresponds to -OH stretching, while a 2915 cm^{-1} represent C-H stretching that characterizes polysaccharides compounds. Also, it showed a 1630 cm^{-1} band that represented the vibration of the absorbed water molecules into the cellulose. The bands present in 1428 cm^{-1}, 1367 cm^{-1}, 1334 cm^{-1}, 1027 $cm^{-1}$and 896 cm^{-1}corresponding to -CH_2 and -CH, -OH and C-O stretching. The band at 1420 cm^{-1} is associated to the cellulose crystalline structure, while 897 cm^{-1} band is associated with the amorphous part of them [28]. The corresponding lignin compound band is found between 1725 cm^{-1} and 1250 cm^{-1}, this is because of the stretching C-C of the benzene ring present in them.

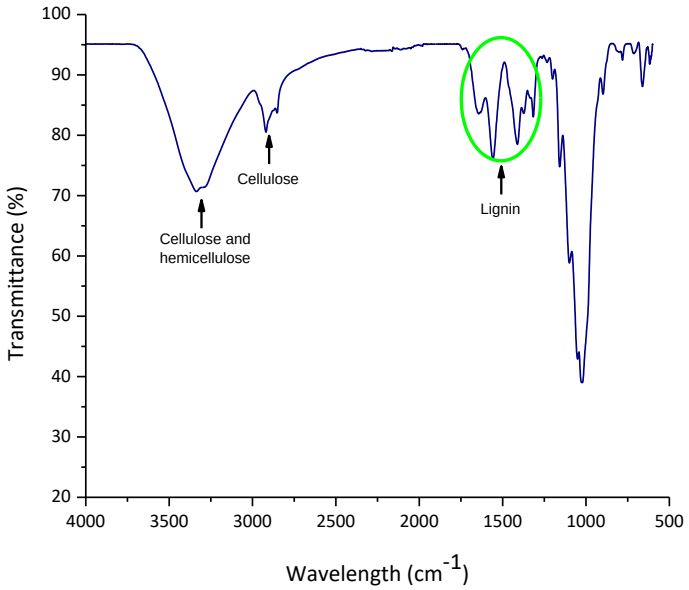


Figure.1. FTIR spectra of banana rachis and peaks obtained

3.3. ***Thermo gravimetric analysis (TGA):*** TGA analysis is a destructive technique that measures the material mass loss with respect to temperature under different inert atmospheres. The TGA curve works for determining the compounds present in the sample, and the percentage that exists of each of them. Figure 2, shows the TGA curve for banana rachis cellulose. 3 important mass losses are observed. The first loss is found between 40 °C and 130 °C, this section represents the rachis samples residual moisture and the occluded water. The loss magnitude is determined by the initial moisture material and this has a value of 2,47% according to Figure 2.

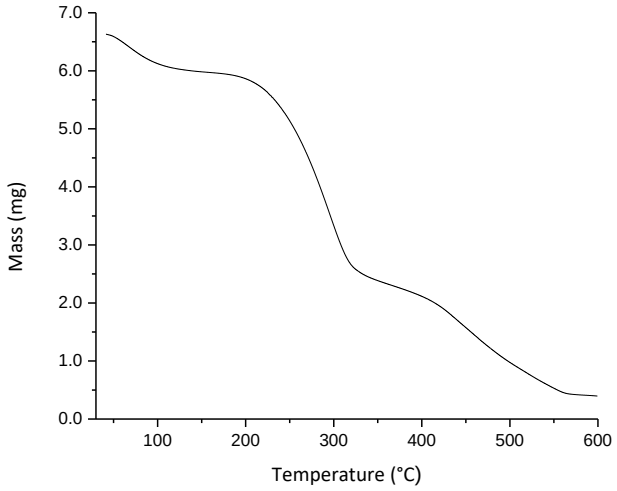


Figure.2. TGA for cellulose obtained from banana rachis

The second mass loss is found between 170 °C and 350 °C, this is attributed to the degradation of the carbohydrates, that is, holocellulose (cellulose + hemicellulose), that corresponds to 16,12%. Finally, the third decrease in the TGA curve is found between 390°C and 579°C that corresponds to lignin degradation. The curves obtained are similar to the Ibrahim et al (2010) and Quoc Lam et al (2001) curves. In these cases,the greater part of holocellulose is degraded before 300°C is reported and this is attributed to low molecular weight carbohydrates degradation. On the other hand, the fast lignin degradation is due to the sample´s high purity[30]-[32]. The curve presented in Figure 2 shows the lignin percentage of 7,49%, this percentage represent 48,01% the lignin in the banana rachis, according the Table 1. Which means that the method is effective to remove lignin from the material.

3.4. ***Confocal laser scanning microscopy (CLSM)***

By confocal laser scanning microscopy, the different parts of the fiber can be seen, cellulose (blue color) and lignin (green color). In Figure 3A and 3B, it shows the fibers without treatment.In Figure 3A a cellulose low fluorescence can be seen. In Figure 3B, the combined lignin and cellulose, the fiber mostly covered by lignin is observed. In Figure 3C and 3D, when basic hydrolysis is performed, there is a greater exposure of the cellulose in the fiber and, therefore, a reduction in lignin is clearly indicated.

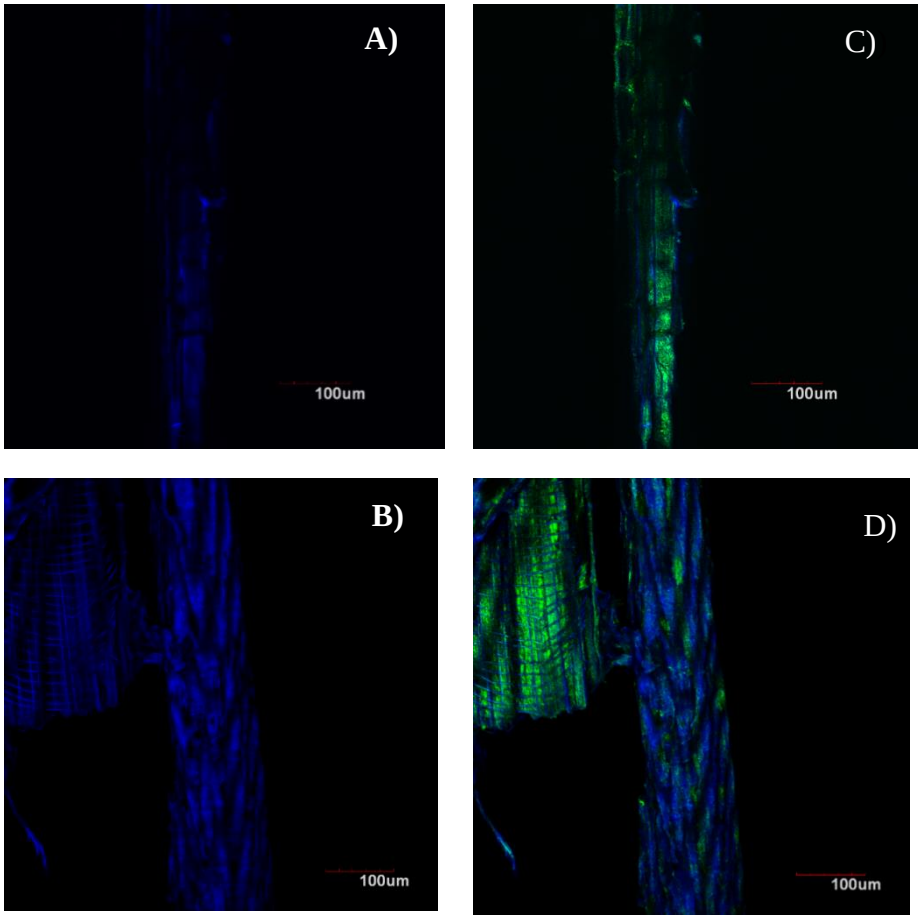


Figure.3.Confocal laser microscopy images without treatment (A and B) and after basic hydrolysis (C and D). the cellulose in blue color and lignin in green color.

3.5. *X-ray diffraction (XRD)*

The X-ray diffraction shows crystallinity degree in one material, this crystallinity degree is found by Crystallinity Index (CI), which is defined as the volume fraction of crystallinity phase in one specific sample and it is defined by the Equation1.

$$CI = \left(\frac{I_{200} - I_{am}}{I_{200}} \right) \cdot 100 \quad (1)$$

Where I_{200} corresponding to crystalline peak magnitude and I_{am} to the valley between amorphous and crystalline peaks [33], [34]. The Figure 4 show cellulose diffractogram obtained.

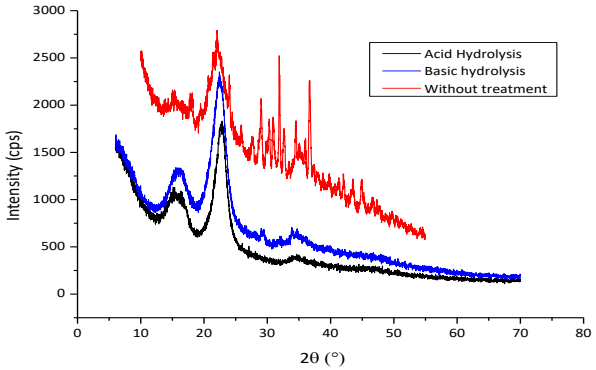


Figure.4. Cellulose diffractogram obtained from banana rachis

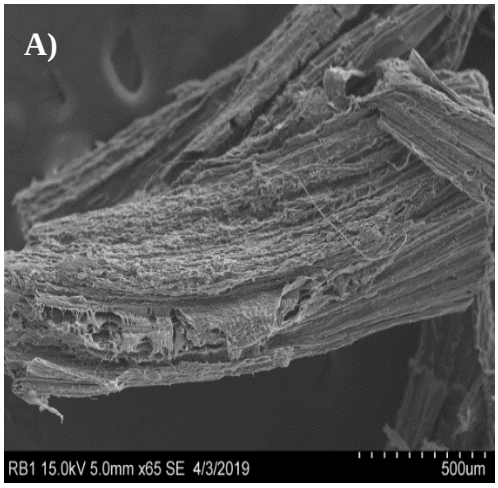
According to Figure 4, the (CI) was calculated (Table 2) using crystalline and amorphous peaks intensity. This Table shows the fiber without treatment has a CI of 35,85%, when basic treatment is added to remove extractives and lignin, the crystallinity was increasedby 23,51%. While the crystalline difference between basic treatment and the second hydrolysis (acid hydrolysis) increased the CI only 4,96%. This difference is not very high because the result is cellulose nanofibrils and not cellulose crystals, being fibers of considerable length, they maintain their amorphous structure.

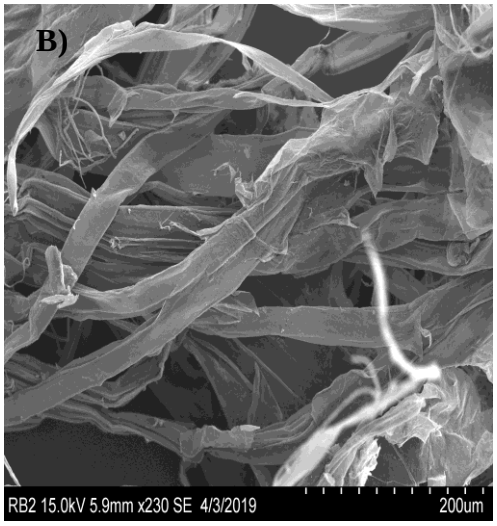
Table.2. Crystallinity index for cellulose from banana rachis

Treatment	CI (%)
Without treatment	35,85
Basic hydrolysis	59,36
Acid hydrolysis	64,32

3.6. *Scanning electronic microscopy (SEM)*

According to the scanning electronic microscopy presented in Figure 5, it shows one morphologic difference in the fibers. When banana rachis aretreated with basic hydrolysis (NaOH) it shows a decrease in fiber size. Although, with just this treatment the fibers have sizes between 250-350 µm, and gummy material and tannins adhered to the fiber. When the bleaching is applied after basic hydrolysis, a decrease in the fibers size occurred and it changed to 20-50 µm, by the tannins elimination. Acid hydrolysis added after treatment applied before, the fibers start to separate and the change in size is not observed. Also, in Figure 6 it can be seen that each treatment added produced asmoother surface, which can be rationed with entropy value calculated by image analyzer *ImageJ*. In this case, an entropy reduction is observed among basic hydrolysis (first step) and bleaching (second step). While, between bleaching and acid hydrolysis (third step) there are changes, but a minor change compared to the previous one. In the same way, this can be corroborated in the figure after acid hydrolysis application because the fibers scales are eliminated.





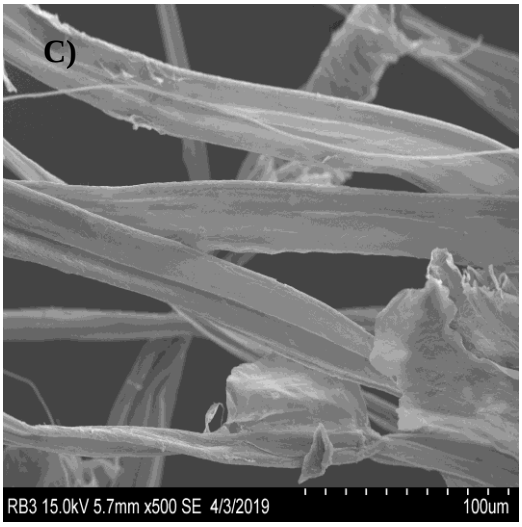


Figure.5. Banana rachis scanning electronic microscopy with different treatments A) Basic hydrolysis B) Bleaching C) Acid hydrolysis

3.7. Transmission electronic microscopy (TEM)

When the mechanical treatment (rupture method) to cellulose is applied, cellulose nanofibrils (NFC) are obtained havinga size of 10-25 nm, according the TEM in Figure 6. Although NFC length are varied. Since they are nanofibrils, they keep the amorphous part that acid hydrolysis cannot to remove. Nevertheless, acid hydrolysis has a positive effect in the fibers cleaning, since it leaves them individually separated,which facilitates the rupture on a nanometric scale.

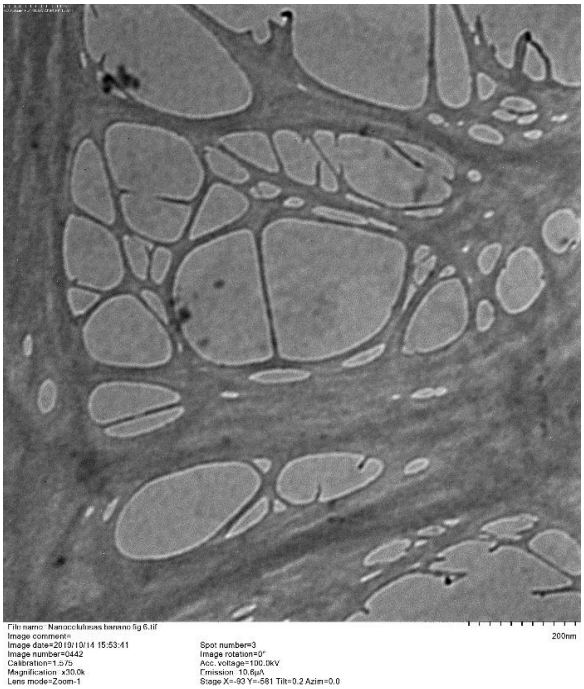


Figure .6. Cellulose nanofibrils transmission electronic microscopy

4. CONCLUSIONS

The banana rachis used as raw material contained 33, 5±1,2% of cellulose and 15,6±1,1% of lignin. After the chemical treatment the51, 99% of total ligninremoved. According to the acid

treatment, the final CI was 64,32%, improving 28,47%. The cellulose obtained has a fiber size between 20-50 µm after basic hydrolysis and whitening, once the breakdown, nanofibrils of 10-25 nm are obtained.

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