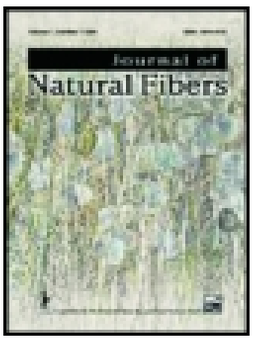

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Utilization of Areca Nut Leaf Sheath Fibers for the Extraction of Cellulose Whiskers

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ABSTRACT

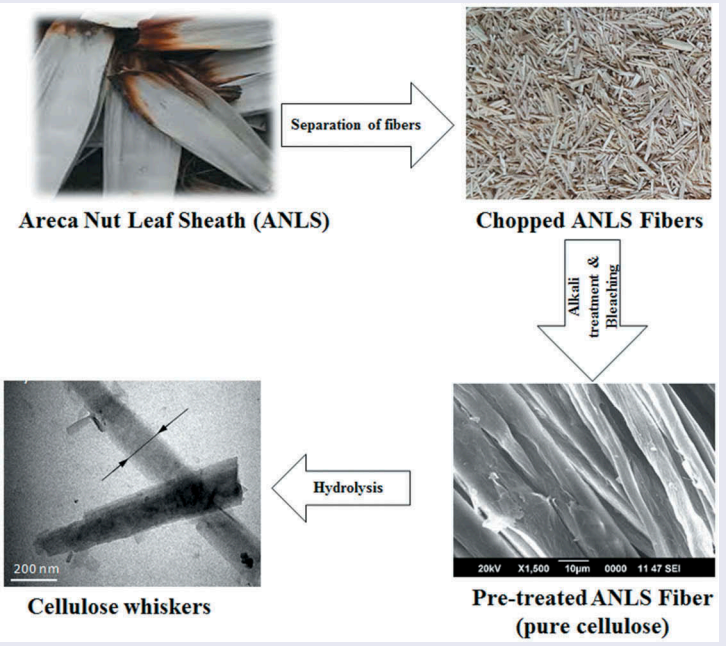
In this study, cellulose whiskers were extracted from an agricultural plant waste, Areca Nut Leaf Sheath, by employing a sulfuric acid hydrolysis method. The effect of hydrolysis time and temperature on the morphology, crystallinity, and degree of polymerization of the resultant cellulose particles was studied. Highly crystalline cellulose whiskers with an aspect ratio around 20 were obtained under moderate conditions of hydrolysis by maintaining the temperature at 45°C and hydrolysis time of 180 min. However, on increasing the temperature and time of hydrolysis, surface flattening of fibers was observed and aspect ratio was decreased. Isolated cellulose whiskers were found to contain traces of biosilica.

KEYWORDS

Areca nut leaf sheath fibers; cellulose whiskers; acid hydrolysis; effect of hydrolysis conditions; degree of polymerization; biosilica

关键词

槟榔叶鞘纤维; 纤维素晶须; 酸水解; 水解条件的影响; 聚合度; 生物矿化硅



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摘要
本研究采用硫酸水解法从农业植物废弃物槟榔叶鞘中提取纤维素晶须研究了水解时间和温度对纤维素颗粒形貌、结晶度和聚合度的影响在中等水解条件下，将水解温度保持在45℃，水解时间保持在180分钟，得到长径比在20左右的高结晶纤维素晶须但随着水解温度的升高和时间的延长，纤维表面逐渐变平，长径比减小分离出的纤维素晶须含有微量的生物硅.

Introduction

In today's world, there is a high demand for products that are biodegradable, environmentally friendly, and derived from non-petroleum based renewable resources. In this perspective, cellulose, the most abundant biopolymer on earth, has attracted much attention. Numerous studies highlight the importance and potential applications of cellulose in various fields (Adel et al., 2016; Elanthikkal et al. 2017; Grishkewich et al. 2017; Habibi, Lucia, and Rojas 2010; Jonoobi et al. 2015). The interesting features of cellulose are its high crystallinity, acceptable specific strength properties, high strength/weight ratio, low density, biocompatibility, biodegradability, non-abrasive nature, renewable source, and economic availability. The utilization of cellulosic fibers as reinforcement offers a large potential for energy savings and reduction of environmental impact (Ramesh, Palanikumar, and Reddy 2017). The reinforcing potential will be high if cellulose in the nano-dimension is used in composite fabrication because of its higher surface area and better filler matrix interaction. Cheap resources like agricultural residue, industrial bio-residue, annual plants have attracted much interest as an economic and worthy source for extracting nanocellulose (Adel et al., 2016; Jonoobi et al. 2015; Vestena et al. 2016). Compared to wood, the percentage of lignin and hemicellulose are low in agricultural residues. Moreover, the use of the industrial and agricultural bio-residues as another valuable material contributes to solving waste disposal problems (Jonoobi et al. 2015).

Among the different methods employed, acid hydrolysis is the most common practice for the isolation of nanocellulose from plant fibers. When pure cellulosic material undergoes intense hydrolysis by a suitable acid under controlled conditions of time, temperature, and mechanical agitation, the amorphous regions of cellulosic fibers undergo scission and produces cellulose micro or nanocrystals called cellulose whiskers. The features of the derived cellulose whiskers generally depend on the type of the acid used, its strength/concentration, the acid to cellulosic material ratio, and also on reaction time and temperature (Dong, Bortner, and Roman 2016; Rosa et al. 2010). In most hydrolysis reactions, the concentration of sulfuric acid ranges from 60 to 65 wt% and the temperature varies from room temperature to 72°C with respect to the hydrolysis time and the source material (Elazzouzi-Hafraoui et al. 2008; Habibi, Lucia, and Rojas 2010). Lee et al. (2017) studied the effect of acid hydrolysis time on the characteristics of nanocellulose isolated from *Eucalyptus globulus* and reported the optimum time condition as 45 min that resulted in highly crystalline cellulose in reasonable yield. Yang et al. (2017) analyzed the effect of extraction methods on the features of nanocellulose produced from corn husk. Authors used sulfuric acid hydrolysis, ultrasonication or TEMPO-oxidation for extracting nanocellulose and reported that nanocellulose produced by hydrolysis possesses high crystallinity and thermal stability.

Areca nut (*Areca catechu*) leaf sheath (ANLS) fiber is a rich source of α-cellulose. As per one report, ANLS fibers contain 75% α-cellulose (Arifuzzaman Khan et al. 2012) and another study reports 66% (Poddar et al. 2016). From the literature survey conducted, no one has yet reported the isolation of nanocellulose from *areca nut leaf sheath fibers*. Julie Chandra, George, and Narayanankutty (2016) have isolated cellulose nanofibrils from *areca nut husk fibers* by a combined chemical and mechanical method. Chemical method involved treatment with alkali,

hydrochloric acid solution, and sodium chlorite. Mechanical treatment involved grinding and homogenization. Compared to areca nut husk fibers, which contain only 34–35% cellulose, areca nut leaf fibers found to possess higher cellulose content (Julie Chandra, George, and Narayanankutty 2016). There are a few reports where ANLS fibers, in the short fiber form, have been used as reinforcement in various polymer matrices (Arifuzzaman Khan et al. 2012; Jayamani et al. 2014; Padmaraj et al. 2013). The present study makes use of this ANLS renewable agricultural resource for the preparation of cellulose whiskers. Kerala, being a major producer of areca nut, a huge amount of this plant waste is being dumped to the land. It is noteworthy to improve the utility of this waste product by converting it into a value-added reinforcing material. The work employs a sulfuric acid hydrolysis method for the isolation of nanocellulose. The effects of hydrolysis temperature and hydrolysis time on the characteristics of the resultant cellulose particles have been investigated.

Materials and methods

Materials

The areca nut leaf sheaths were collected from areca nut tree of local area of Kerala, India (Malappuram). The fibers separated from ANLS were washed, dried, chopped and finely ground in a blender. The ground fibers were sieved and used for the isolation of cellulose. Sulfuric acid was purchased from Sigma Aldrich. The other chemicals used in this study were of analytical purity.

Isolation of cellulose whiskers from areca nut leaf sheath fibers

Initially, the components present in ANLS fibers were estimated by the methods described elsewhere (Arifuzzaman Khan et al. 2012). Prior to hydrolysis, the associated components like lignin, hemicelluloses present in the ANLS fibers were removed by an alkali treatment and bleaching steps as described in our previous study (Elanthikkal et al. 2010). The pure cellulose residue obtained after the pre-treatment was subjected to controlled acid hydrolysis, using 64 wt% sulfuric acid solution. To study the effect of hydrolysis temperature and time on the characteristics of the cellulose whiskers, hydrolysis was performed at two different temperatures, 45°C and 65°C, for two reaction times as 90 and 180 min (sample coding is given in Table 1). At the end of the reaction, hydrolysis reaction was arrested by diluting the reaction mixture to ten-fold with ice-cold distilled water. The dispersion was centrifuged and washed repeatedly, and the stable aqueous suspension of cellulose whiskers obtained was freeze dried.

Fourier transform infrared spectroscopy (FTIR)

FT-IR spectra of fibers and cellulose whiskers were analyzed using a Varian 630 FT-IR spectrometer. Spectra were taken in the transmittance mode in the wavenumber range of 450–4000 cm^{-1}, at 4 cm^{-1} resolution.

Table 1. Sample coding used for the cellulose whiskers produced by hydrolysis of ANLS fibers.

Sample code	Hydrolysis temperature (°C)	Hydrolysis time (min)
Cellulose-T_{45} t_{90}	45	90
Cellulose-T_{45} t_{180}	45	180
Cellulose-T_{65} t_{90}	65	90
Cellulose-T_{65} t_{180}	65	180

X-ray diffraction studies (XRD)

XRD measurements of fibers and hydrolyzed cellulose whiskers were performed on a Bruker AXS D8 Advance X-ray Powder Diffractometer. The diffracted intensity of Cu Kα radiation (0.154 nm) was measured in a 2θ range between 5° and 70°. Crystallinity index was calculated by peak height method using Segal equation (Equation 1). In Equation 1, I_{002} is the intensity of (002) diffraction peak (at 2θ = 22.5°), I_{am} is the intensity of amorphous peak (min peak at 2θ ~ 18°) (Karimi and Taherzadeh, 2016).

$$CrI = \frac{I002 - Iam}{I002} \times 100 \tag{1}$$

The crystallite size (L_{002}) was obtained through the Scherrer's formula (Equation 2).

$$L_{002} = \frac{k\lambda}{\beta 002\ \cos\theta} \tag{2}$$

where k (Scherrer constant) is 0.9 for cellulose, λ is the X-ray wavelength (0.154 nm), and β_{002} is the lattice peak width at half its intensity.

Calculation of degree of polymerization and viscosity average molecular weight

Intrinsic viscosity of cellulose samples prepared under different conditions was determined based on ASTM D-4243-99. Definite amount of cellulose was dissolved in 0.5 M cupriethylene diamine solution. The time of flow of the cellulose solution and the solvent were measured using viscometer. Specific viscosity η_s is determined by applying Equation (3).

$$\eta_s = t_s - t_o / t_o \tag{3}$$

where t_s is the mean flow time of the solution and t_o is the mean flow time of the solvent. Knowing the value of η_s and the concentration c in g/100 ml, the value of intrinsic viscosity [η] is obtained as:

$$[\eta].c = [\eta_s] \tag{4}$$

The average viscometric degree of polymerization, DP is given by Equation (5).

$$DP^{\infty} = [\eta]/K, \tag{5}$$

where ∞ = 1 and K = 7.5 x 10^{-3}

Scanning electron microscopy (SEM)

Surface morphological features of the fibers and cellulose whiskers were analyzed using scanning electron microscope (JEOL Model JSM – 6390LV; FEI, ISPECT S50, Czech Republic). The acceleration voltage was set to 20 kV. The samples were coated with gold using sputter coating machine (Quorum, Q150R ES, UK).

Transmission electron microscopy (TEM)

For transmission electron microscopic analysis, a TEM, FEI, Morgagni, Czech Republic at voltage 80 kV was used.

Particle size analysis and zeta potential measurement

A Malvern Zetasizer Nano-ZS was used to analyze the particle size and zeta potential of aqueous cellulose suspension of the freeze-dried cellulose sample.

Thermogravimetric analysis (TGA)

A Perkin Elmer, STA 6000 (USA), TG/DTA Thermo-gravimetric analyzer was used to study the thermal degradation of untreated and treated fibers, across the temperature range of 30–600°C, at a heating rate of 10°C/min, under nitrogen environment.

Results and discussion

Estimation of main components in areca nut leaf sheath fibers

The composition of natural fibers varies according to their origin. The main components present in natural fibers are cellulose, lignin, hemicellulose in addition to some amount of pectin and other extractives. Before the isolation of nanocellulose from natural cellulosic fibers, it is important to understand the chemical composition and the cellulose content in the fibers. Chemical composition of ANLS fibers was estimated and the obtained data is presented in Table 2. It is interesting to note that the waste fibers contained 72% of cellulose. The moisture content of Areca nut leaf sheath fiber was found to be 9–10% (ASTM D-1348).

FT-IR spectroscopic analysis

FT-IR spectroscopic analysis can be used to ascertain the removal of lignin, hemicelluloses, pectin, etc., from the ANLS fibers by the applied chemical treatments. The FT-IR spectra of untreated ANLS, alkali treated and bleached ANLS (pure cellulose) and cellulose whiskers obtained after hydrolysis (Cellulose-$T_{45}t_{90}$) are shown in Figure 1. The 1731 cm^{-1} peak observed in the spectrum of untreated ANLS fibers corresponds to the acetyl and uronic ester groups of hemicelluloses or to the ester linkage of carboxylic group of ferulic and *p*-coumaric acids of lignin and/or hemicellulose. The peak at 1517 cm^{-1}, in the spectrum of the untreated fibers, represents the aromatic –C=C– stretching of the aromatic rings of lignin. The lack of bands at 1731 cm^{-1} and at approximately 1517 cm^{-1} and 1250 cm^{-1} imply the efficient removal of lignin and hemicelluloses in the treated fibers, by the applied alkali treatment and bleaching (Adel et al., 2016; Yongvanich 2015). The broad band at 3414 cm^{-1} region present in all spectra arises from the stretching of hydrogen bonded –O–H groups in cellulose. The peak at 1636 cm^{-1} region has been attributed to the –O–H bending vibrations. The peak in the 2905 cm^{-1} region corresponds to the stretching – C–H groups of cellulose. The band around 1045 cm^{-1} region arises due to the –C–O–C– pyranose ring skeletal vibration. The small, sharp peak at 893 cm^{-1} represents glycosidic $–C_1–H$ deformation, with a ring vibration contribution and –O–H bending. These features are characteristic of β-glycosidic linkages between the anhydroglucose units in cellulose (Alemdar and Sain 2008; Nagalakshmaiah et al. 2015).

X-ray diffraction studies

XRD analyses have been carried out in order to determine the crystallinity changes of the fibers and to understand the cellulose polymorph. XRD patterns of the untreated ANLS fibers, alkali treated and bleached ANLS fibers (pure cellulose), and cellulose whiskers (hydrolyzed cellulose samples) are shown in Figure 2. The diffractograms, represented a typical cellulose I polymorph, displaying a sharp intense singlet peak around $2\theta = 22.5°$, a shoulder in the region $2\theta = 14–16°$ and a small peak at 35° (French 2014). The higher peak intensity of the bleached ANLS fibers and hydrolyzed cellulose whiskers indicates the

Table 2. Chemical composition of areca nut leaf sheath fibers.

Components	%
Cellulose	72.27
Hemicellulose	13.38
Lignin	12.84
Extractives	1.51

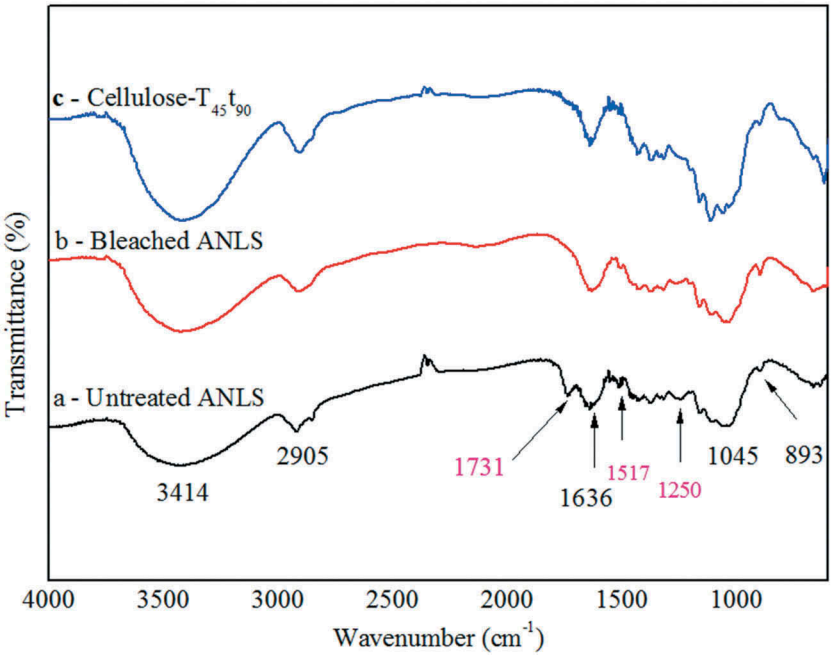

Figure 1. FT-IR spectra of (a) untreated ANLS fibers, (b) alkali treated and bleached ANLS fibers – pure cellulose, and (c) hydrolyzed cellulose whiskers – cellulose-T_{45} t_{90}.

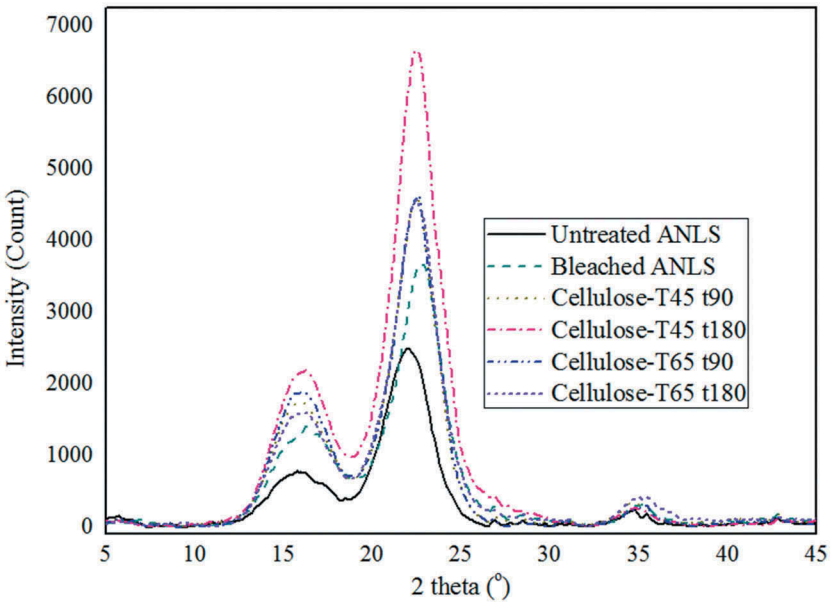

Figure 2. X-ray diffraction patterns of untreated ANLS, alkali treated and bleached ANLS fibers and the hydrolyzed cellulose whiskers.

removal of amorphous regions by the applied chemical treatments (Shaheen and Emam 2018). The crystallinity index (percentage crystallinity) of cellulose whiskers has been calculated using Equation (1) by employing the peak height method and the results are presented in Table 3. Cellulose whiskers exhibited

Table 3. Values of crystallinity index and crystallite size of cellulose whiskers.

Sample	Crystallinity index (%)	Crystallite size (nm)
Cellulose-T_{45} t_{90}	85.50	6.36
Cellulose-T_{45} t_{180}	85.78	5.69
Cellulose-T_{65} t_{90}	85.30	6.05
Cellulose-T_{65} t_{180}	82.40	5.96

very high crystallinity, which varied between 82.4% and 85.7%. A slight reduction in the crystallinity index of the cellulose whiskers has been observed when hydrolysis temperature increased from 45°C to 65°C. This could be due to the fact that the treatment with the sulfuric acid solution at higher temperatures and for longer time, not only affected the amorphous regions, but some crystalline regions in cellulose also underwent cleavage. The crystallite size (thickness) of cellulose whiskers calculated by Scherrer's method is also presented in Table 3. A small decrease in crystallite size of cellulose whiskers was observed when the hydrolysis time increased from 90 to 180 min. Other authors have also made this kind of observation for cellulose whiskers extracted from oil palm by following different hydrolysis time (Saurabh 2016).

Calculation of degree of polymerization and viscosity average molecular weight

Viscometry serves as a reliable tool to determine the degree of polymerization (DP) of cellulose and its derivatives. DP of extracted cellulose whiskers was determined viscometrically as described in the experimental part (Chenampulli et al. 2013). DP value of the cellulose whiskers, produced from ANLS fibers by following different hydrolysis conditions, is displayed in Table 4. When the time of hydrolysis increased, DP value was found to decrease. When temperature of the hydrolysis reaction increased, a greater reduction in DP value was observed, as presented in Figure 3. The reduction in

Table 4. Values of DP and molecular weight of cellulose whiskers.

Sample	Degree of polymerization (DP)	Molecular weight
Cellulose-T_{45} t_{90}	77.97	12631.14
Cellulose-T_{45} t_{180}	49.17	7965.54
Cellulose-T_{65} t_{90}	43.81	7097.22
Cellulose-T_{65} t_{180}	18.86	3055.32

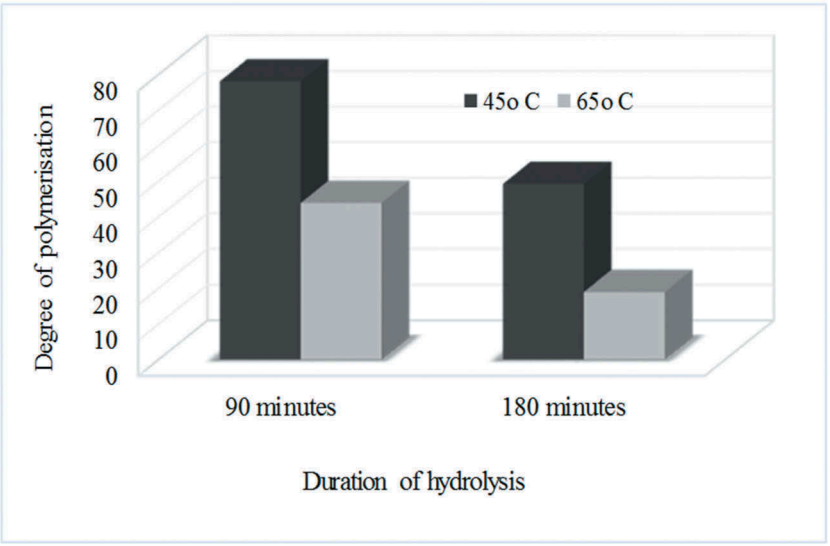

Figure 3. Effect of hydrolysis time and temperature on the degree of polymerization of cellulose whiskers.

DP value and molecular weight indicate that as the duration or temperature of reaction increases, long cellulose chains are breaking down to shorter chains.

Scanning electron microscopic analysis

Figure 4 shows the SEM images of (a) untreated ANLS fiber and (b) alkali treated and bleached ANLS fiber. In the raw fiber, cellulose was found cemented in the matrix of hemicelluloses and lignin. By the applied pre-treatments, the cementing materials got removed and the fibers exhibited a layer type arrangement. Figure 4c–f represents the SEM images of hydrolyzed cellulose whisker

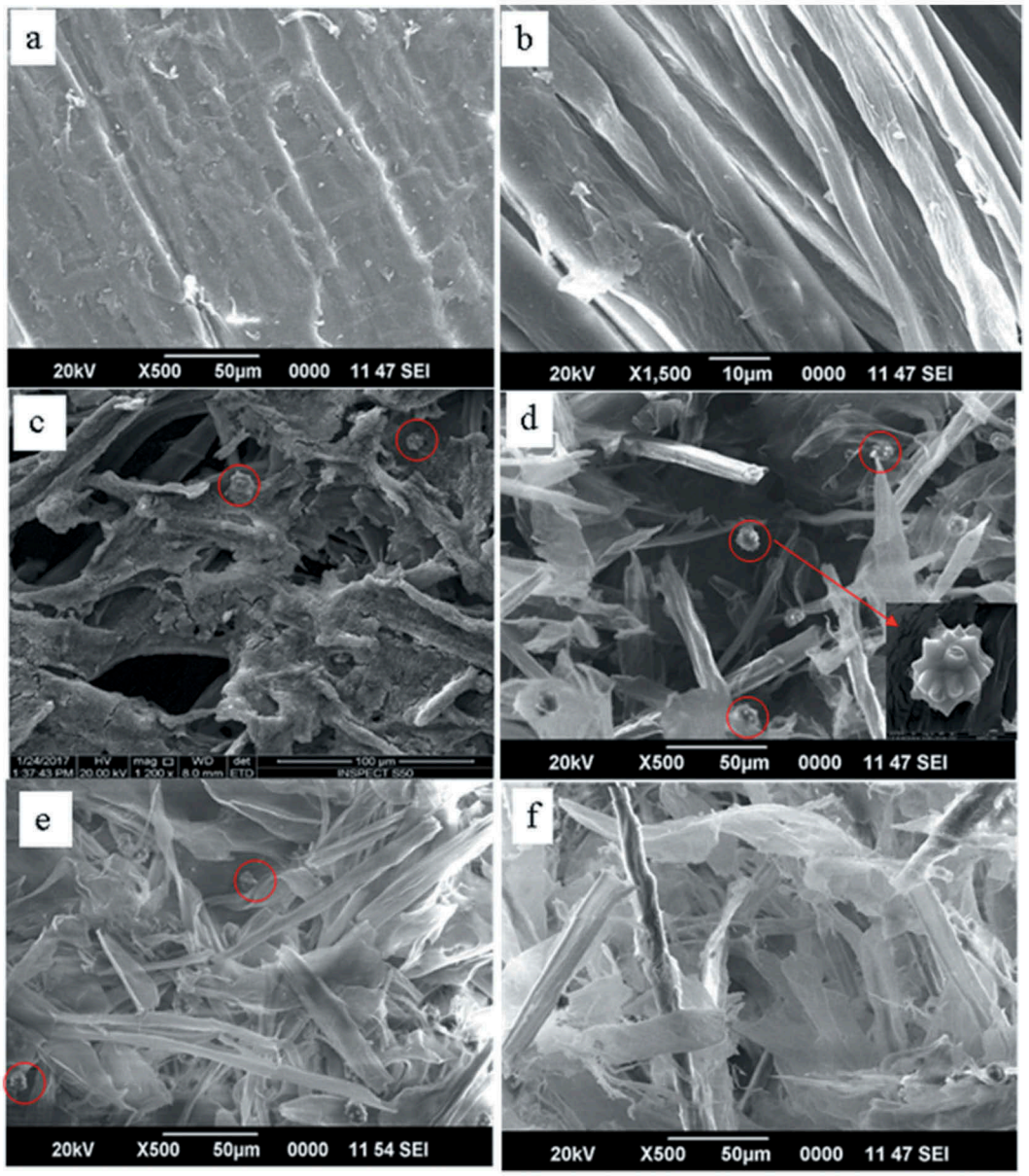

Figure 4. SEM images of (a) untreated ANLS fiber, (b) alkali treated and bleached ANLS fiber, (c) cellulose-T_{45} t_{90}, (d) cellulose-T_{45} t_{180}, (e) cellulose-T_{65} t_{90}, and (f) cellulose-T_{65} t_{180}.

samples prepared under different hydrolysis conditions. During hydrolysis, cellulose chains break down into smaller crystallites. The morphology and size of cellulose particles were influenced by the applied hydrolysis conditions. Long rod-like fibers were obtained at low temperature (45°C) hydrolysis. When the hydrolysis temperature increased, comparatively short fibers with flattened surface were obtained. The cellulose whiskers produced by hydrolysis at 65°C, 180 min (Cellulose-T_{65} t_{180}) exhibited fibrillation generating nanofibrils. It was noticed that a few silica bodies were present at the surface of the cellulose whiskers, as shown in the SEM images. More images showing the presence of flower-like silica bodies on the surface of derived cellulose whiskers are displayed in the supplementary file (Figure S1). The average dimension of the individual silica particle was 4–5 µm. In a recent work, a group has isolated this kind of rosette-like biosilica as a subproduct of nanocellulose isolation process from pineapple peels (Corrales-ureña et al. 2018). Yusriah et al. (2014) also observed these types of trichomes at the surface of areca nut husk fibers and they reported that these trichomes can serve as sites for mechanical interlocking and these fibers can provide better reinforcing effect in polymer composites.

Transmission electron microscopic analysis

Figure 5a_1 & b_1 represents the TEM images, respectively, of cellulose whisker samples Cellulose-T_{45} t_{180} and Cellulose-T_{65} t_{180}. Figure 5a_2 & b_2 represents their intensity profiles. TEM micrographs showed the presence of cellulose in nano dimension. In each image, two cellulose fibers were seen. The intensity profile was extracted in order to measure the thickness and length of the fibers. Interestingly, in Cellulose-T_{45} t_{180} sample, both the cellulose fibers have shown uniform thickness in longitudinal direction. The thickness of the above cellulose sample was measured around 34 nm. On the other

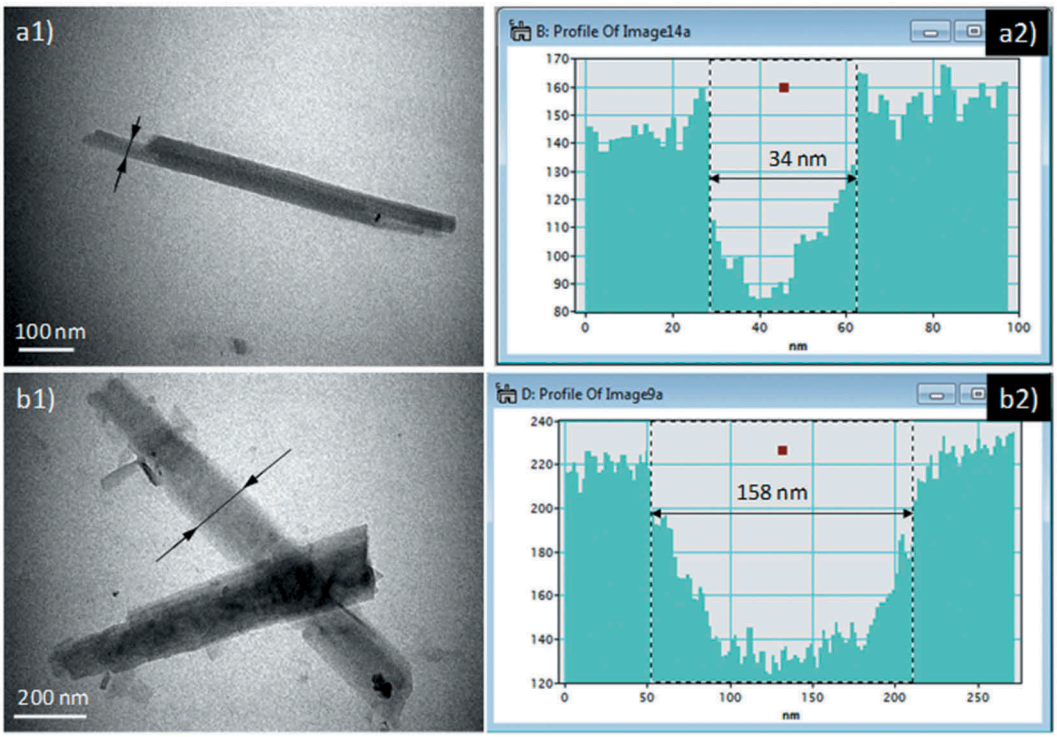

Figure 5. Transmission electron microscopic image of (a_1) cellulose-T_{45} t_{180} and (a_2) its intensity profile, and (b_1) cellulose-T_{65} t_{180} and (b_2) its intensity profile.

hand, in Cellulose-T_{65} t_{180} sample, both the fibers exhibited non-uniform thickness. One side of the fiber was thicker than the other. Therefore, the thicknesses of these fibers were measured at different places and calculated the average value of the thickness to estimate the aspect ratio. Cellulose-T_{45} t_{180} possess long rod-like structure, with high aspect ratio 17–19.7. However, Cellulose-T_{65} t_{180} were flatter as seen in the SEM image, with aspect ratio around 5.9–8.

Particle size analysis and zeta potential measurement

To further confirm the nano dimension of the extracted cellulose whiskers, particle size analysis of Cellulose-T_{45} t_{180} was performed. The particle size distribution of Cellulose-T_{45} t_{180} cellulose sample is shown in Figure 6a. A bimodal distribution of particle size was observed. Sample showed a diameter average particle size of 539.6 nm (peak of maximum intensity).

The zeta potential is commonly used to characterize the surface charge property of nanoparticles. It reflects the electrical potential of particles and is influenced by the composition of the particles and medium in which it is dispersed. Generally, nanoparticles with a zeta potential near ± 30 mV have been shown to be stable in suspension, as the surface charge prevents agglomeration of the particles.

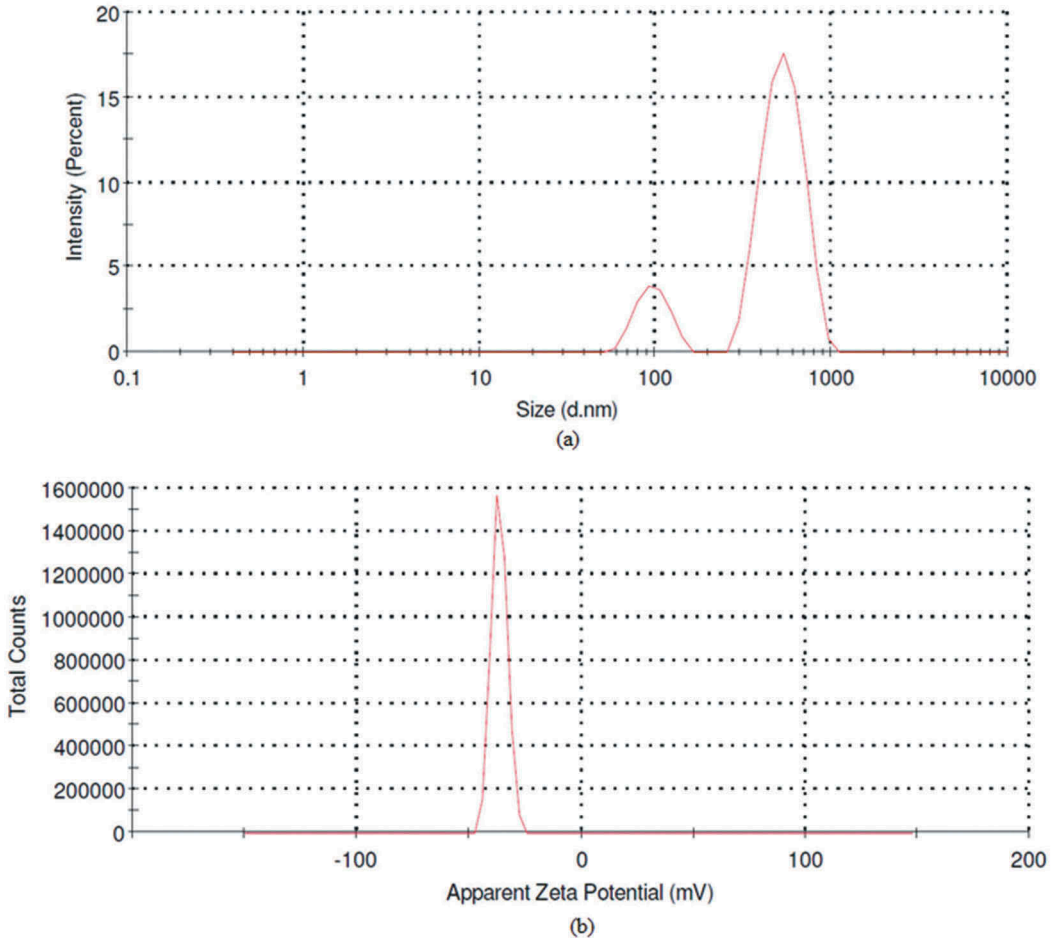

Figure 6. (a) Particle size distribution, and (b) Zeta potential distribution of cellulose whisker (cellulose-T_{45} t_{180}) aqueous suspension.

Zeta potential measurement was carried out on an aqueous dispersion of cellulose whiskers (Cellulose-T_{45} t_{180} sample). The dispersion showed a negative zeta potential value, −40.0 mV (Figure 6b). This highly negative zeta potential value indicates that cellulose has undergone sulfonation and the repulsive interaction between the negatively charged sulfate groups leads to stable suspension.

Thermogravimetric analysis

Figure 7 shows the consequences arising from the heating and subsequent pyrolytic degradation of untreated ANLS fibers and treated ANLS fibers. The initial weight loss during heating to 120°C, corresponds to the vaporization and removal of bound water in the cellulose fibers. The cleavage of the glycosidic linkages of cellulose, leading to the formation of H_2O, CO_2, alkanes and other hydrocarbon derivatives, occurs in the temperature range of 180–370°C. After 380°C, the residual decomposition products maintain a slow degradation profile. From the figure, it can be seen that the onset degradation temperature of treated fibers has shifted to higher temperatures. The hemicelluloses, lignin, and pectin present in the raw fibers, which possess low decomposition temperature, were removed by the applied treatments, and the bleached, hydrolyzed cellulose fibers exhibited higher thermal stability (Moubarik, Grimi, and Boussetta 2013). Treated fibers showed higher percentage of residue, which could be due to the presence of bio-silica content, as seen in the SEM images.

Conclusions

Areca nut leaf sheath fibers have been identified as a potential source for the extraction of nanocellulose. The determination of chemical composition of ANLS fibers revealed the presence of 72% cellulose. Cellulose whiskers were isolated from the pre-treated ANLS fibers by an acid hydrolysis method. FT-IR spectroscopic analysis and XRD analysis of the samples revealed the

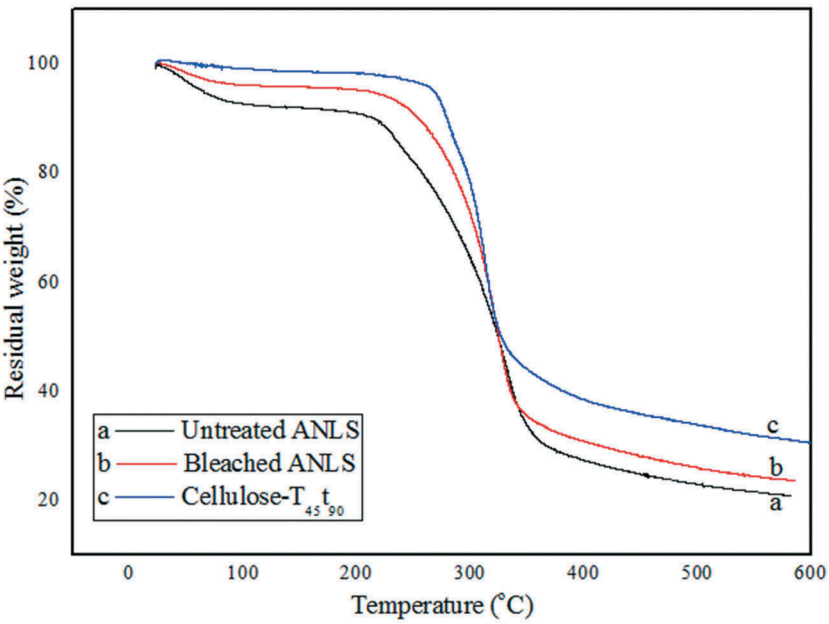

Figure 7. Thermogram of (a) untreated ANLS fibers, (b) bleached ANLS fibers, and (c) hydrolyzed cellulose whiskers (cellulose-T_{45} t_{90}).

effective removal of lignin, and hemicelluloses by the applied chemical treatments. Effect of hydrolysis temperature and duration of hydrolysis on the characteristics of the isolated cellulose whiskers has been studied. Rod-like cellulose whiskers with comparatively high aspect ratio were obtained by low-temperature hydrolysis, i.e., at 45°C. However, when the temperature and time of hydrolysis increased, surface erosion of fibers was observed, and aspect ratio decreased. TEM analysis and particle size analysis confirmed the nano-dimension of cellulose whiskers. The crystallinity index of the various samples of cellulose whiskers synthesized under different conditions varied between 82.4% and 85.7%. DP and molecular weight of cellulose particles were found to depend on the hydrolysis conditions used. Longer reaction time and higher hydrolysis temperature caused the breaking up of cellulose chains and thus low DP value. It was interesting to note that the extracted cellulose particles contained some amount of flower-like silica bodies in it. This biosilica contained cellulose whiskers would be a promising reinforcing material to develop nanocomposites for biomedical and other structural applications.

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