EXTRACTION AND CHARACTERIZATION OF NANOCELLULOSE FROM *PONGAMIA PINNATA* OIL MEAL

DIVYA NATARAJ,[*] CHUNYAN HU[**,***,****] and NARENDRA REDDY[*]

[*]*Center for Incubation, Innovation, Research and Consultancy, Jyothy Institute of Technology, Thathaguni Post, Bengaluru 560082, India*
[**]*College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, People's Republic of China*
[***]*National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 201620, People's Republic of China*
[****]*National Cashmere Products Engineering and Technical Research Center, Erdos Cashmere Group, Ordos 017000, Inner Mongolia, People's Republic of China*
✉ *Corresponding author: N. Reddy, narendra.r@ciirc.jyothyit.ac.in*

Received September 10, 2021

Studies on cellulose/nanocellulose obtained from oil meals are very limited, but present interest and have scientific significance, since the structure, properties and performance may be different from those of other cellulose or nanocellulose types. Thus, the main objective of this work was to extract nanocellulose from an unconventional source – oil meal. Oil meals contain about 20-25% carbohydrates, but the structure and properties of the cellulose from oil meals has not been reported so far. In this research, we have extracted nanocellulose (particles and fibers) from *Pongamia pinnata* oil meal by alkali treatment, bleaching, and acid treatment. The cellulose obtained after bleaching and the final nanocellulose achieved after acid treatment were thoroughly characterized to determine their composition, structure and properties. Morphological studies using TEM and AFM proved the presence of nanostructures in the form of nanoparticles and nanorods. The average effective diameter and mean zeta potential, according to dynamic light scattering experiments, were found to be 338 nm and -13.3 mV, respectively. The weight average molecular weight and degree of polymerization obtained from SEC MALLS were 54,300 and 335, respectively. Higher thermal stability and reduced crystallinity of nanocellulose, in comparison with cellulose, were observed. Overall, a comparative report on the characterization of nanocellulose extracted from *Pongamia pinnata*, with its respective cellulose, has been provided here.

Keywords: *Pongamia pinnata*, oil meal, cellulose, nanocellulose

INTRODUCTION

Cellulose is the major constituent of almost all the plants and hence, it is one of the most abundant natural resources on earth. It is constantly replenished by photosynthesis and hence forms about half to one-third of plant tissues. Cellulose is a biopolymer that is biodegradable, low cost and renewable, in addition to being a non-toxic material.[1] Due to its properties and availability, cellulose has been used in various forms for innumerable applications. In recent years, nano-sized cellulose, or nanocellulose with sizes ranging from 10 nm to 350 nm, has drawn much research attention.

The extraction of nanocellulose from various sources has been investigated.[2] Though several conventional sources, such as wood, are used for nanocellulose production, in the last few years, researchers have attempted using cellulosic waste, particularly agricultural residues, for developing nano-based bioproducts. Agricultural residues, such as rice husk,[3] coconut husk fibers, sugarcane bagasse,[4] cassava bagasse, sisal fibers,[5] soybean pods, corn stalks, kenaf and wheat fibers,[6] jute fiber waste, raw cotton linter,[7] waste tissue paper,[8] *etc*., have been studied for the extraction of nanocellulose. However, the extraction conditions have been varied based on the raw material used and, subsequently, different forms of nanocellulose, such as nanocrystals, nanowhiskers, nanofiber, microcrystals,

nanocrystalline cellulose or monocrystals, have been obtained.[9]

Several different approaches have been used for the extraction of nanocellulose. Mechanical treatments, such as homogenizing at high pressure,[10,11] chemical treatments, such as acid hydrolysis[12,13] and alkaline treatment, as well as biological treatments like enzymatic hydrolysis[14] have been adopted. The mechanical treatment has its advantages, allowing to obtain enhanced fibrillation and uniformly sized fibers. Similarly, chemical treatment, such as acid hydrolysis, consumes less energy and leads to easy recovery of chemicals.[15] However, these methods also have some disadvantages, for example, mechanical treatment involves high energy consumption and causes mechanical damage to the crystalline structure. Chemical treatments also pose problems, such as high consumption of chemicals and generation of acid/alkali waste, which in turn leads to health hazards.[15,16] Enzymatic hydrolysis requires long reaction times because of the mild reaction conditions involved.[15] Therefore, considering the drawbacks associated with each method, a combination of a number of them would be preferred for nanocelulose extraction.

Some of the most attractive properties of nanocellulose include its high stiffness, aspect ratio and strength, its low density and easy biodegradability.[17,18] Also, the liquid crystal property, which enables nanocellulose to demonstrate chiral nematic self-ordering in non-polar solvents,[19] is of great commercial importance. In addition to the above-mentioned characteristics, nanocellulose is of research significance due to its renewability and availability, unique morphology, light weight with high crystallinity, and small particle size.[16]

There are numerous possible applications of nanocellulose across diverse industries. It is used in packaging applications, in cosmetics, in the food industry, in hygiene and adsorbent products, in the medical and pharmaceutical industry *etc*. It has been reported useful in manufacturing high-quality paper products,[20] in cosmetics as a thickener,[21] and in the food industry as a stabilizer,[22] fat replacer and texturing agent; in moldable lightweight, high strength materials; in novel materials for electronics and pharmaceutical applications.

While, as mentioned above, a wide range of natural sources have been investigated in detail for nanocellulose production, the usage of oil meal (by-product of oil/biodiesel production), which also contains cellulose, has not been explored so far. *Pongamia pinnata*, a leguminous, N_2-fixing tree, is native to India. *Pongamia* seeds are a rich source of oil (28 to 42%) and are successfully used for preparing biodiesel. This non-edible oil is of medicinal value and finds applications in biofuel, biogas, and electricity production. Once the oil is removed from the seeds, the deoiled seed cake contains a high amount of crude proteins (30%), which can be utilized for many applications.[23,24] The oilseed cake (75% of seed weight) is obtained as a by-product after extracting the oil. The cellulose, in the case of these oil meals, may be different in terms of structure and hence performance, compared to those obtained from conventional sources.

This paper reports for the first time the extraction of nanocrystalline cellulose from *Pongamia pinnnata* oil meal and the properties of the nanocellulose extracted. Both acid hydrolysis and alkaline treatment methods were used for the extraction. The obtained nanocellulose was characterized to provide an insight into its morphology, changes in functional groups, in comparison with the original cellulose, thermal stability, particle size, and zeta potential. Besides, viscosity studies were carried out to determine the molecular weight of the nanocellulose extracted.

EXPERIMENTAL

Materials

Pongamia oil meal was obtained from Gandhi Krishi Vignan Kendra, Bangalore, India; sodium hydroxide was purchased from Thomas Baker Pvt. Ltd., acetic acid and sulphuric acid – from Nice Chemicals Pvt. Ltd., sodium chlorite – from Loba Chemie Pvt. Ltd. Distilled water was used throughout the experiment and all the chemicals were used without any further purification.

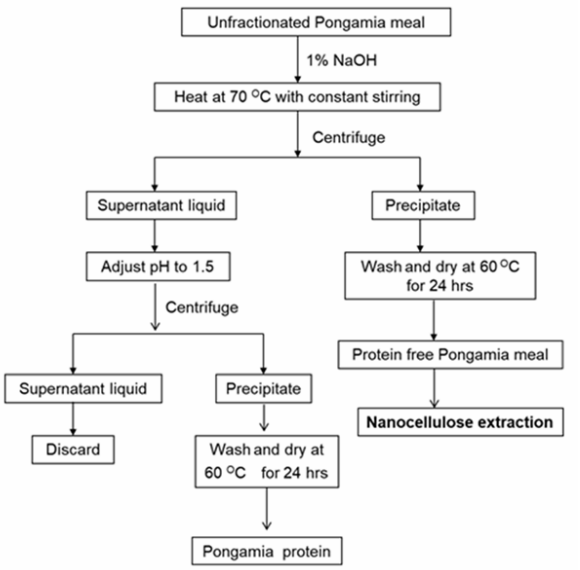
Methods

Extraction of protein-free Pongamia pinnata *portion*

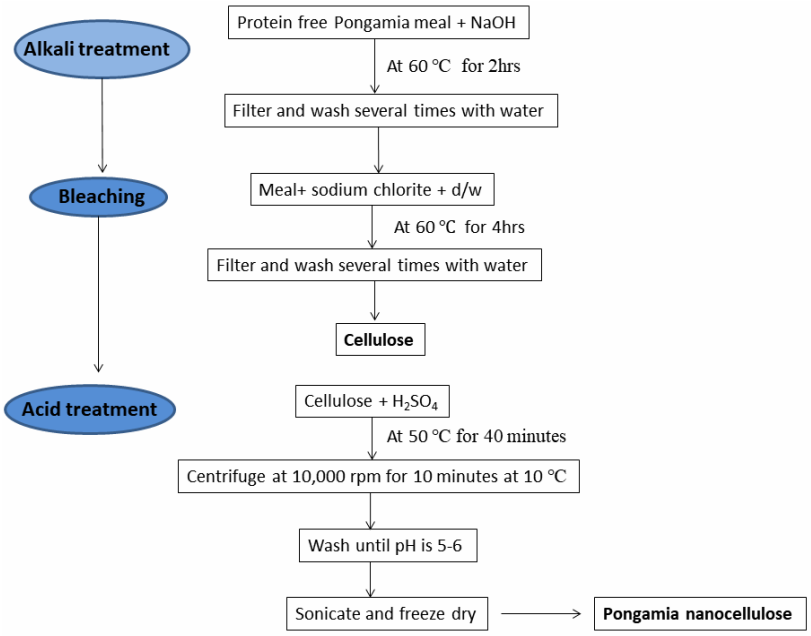
Powdered *Pongamia pinnata* oil meal was treated with 1% NaOH solution at 70 °C under constant stirring for 60 minutes. The ratio of the *Pongamia* meal to the alkali solution was 1:4. After treatment, the sample was centrifuged at 8000 rpm for 15 minutes. The obtained precipitate was collected, washed with distilled water multiple times and dried at 60 °C for 24 h.[25] This protein-free portion, rich in cellulose, was further used for nanocellulose extraction. A schematic depiction of the process used to extract the protein-free portion of *Pongamia* meal is shown in Scheme 1.

Preparation of nanocellulose from* Pongamia pinnata *oil meal

The procedure followed for the extraction of nanocellulose was similar to the protocol followed by Johar,[3] with slight modifications,[3] and it is depicted in Scheme 2. Briefly, the cellulose was processed to remove lignin and hemicelluloses, followed by alkali treatment using sodium hydroxide (4%). The bleaching process was carried out with the addition of acetic acid, sodium chlorite, and distilled water for 4 h at 60 °C. The mixture was cooled and filtered using excess distilled water. Later, the dried filtrate was treated in 10 mol^{-1} L H_2SO_4 for 40 minutes under continuous stirring. The above mixture was washed with distilled water at 10,000 rpm 10 °C for 10 minutes until the pH was between 5-6. The resulting suspension was sonicated for 30 minutes and freeze-dried to obtain solid nanocellulose.



Scheme 1: Flow chart showing the extraction of protein-free *Pongamia* portion



Scheme 2: Procedure followed for the extraction of nanocellulose from protein-free *Pongamia pinnata* oil meal

Morphology studies

Transmission electron microscopy (TEM) (JEOL JEM-2000EX) and atomic force microscopy (SPA 300) were used to determine the morphology of the cellulose nanofibers/nanoparticles. TEM images of the cellulose sample were captured at an accelerating voltage of 200 kV. The cellulose fibers were dispersed in distilled water (0.05 wt%) and sonicated in an ultrasonic bath for 2 min. A drop of sonicated solution was dropped on the sample grid before drying under ambient conditions. Before observation, a drop of 3% uranyl acetate was used to stain the sample. The excess staining solution was removed using filter paper and the sample was allowed to dry. The dried sample was then observed by TEM and images were taken at different magnifications.

The morphology of *Pongamia* nanocellulose was also captured using a SPA 300 AFM (SII NanoTechnology Inc., Japan) scanning probe system. Samples were prepared by dispersing the cellulose nanofiber (0.05 wt%) in distilled water. The samples were then carefully dropped on freshly cleaved mica, using a micropipette, and allowed to dry under ambient conditions. AFM images were taken in the tapping mode and the distribution was analyzed. The thickness of the fibers was calculated as the difference between the mica surface and the nanofibers using Spisel32 software. At least 25 points were considered before reporting the average value with ± one standard deviation.

Particle size and zeta potential analysis by dynamic light scattering

Particle size was measured by laser diffractometry using a Nano Size Particle Analyzer (ZEN 1600 Malvern, USA), in the range between 0.6 nm and 6.0 µm, under the following conditions: particle refractive index 1.450, water refractive index 1.33, viscosity 0.890 cP, temperature 25 °C. Five measurement cycles of 10 s each were taken and the average was calculated using software (Zeta Pals particle sizing software Ver5.23). The above equipment uses dynamic light scattering to measure the diffusion of particles moving in Brownian motion and converts this into size and size distribution. The particle size was measured using the Smoluchowski algorithm. It also uses laser Doppler microelectrophoresis to apply an electric field to the dispersion of particles, which then move with a velocity related to their zeta potential.

SEC-MALLS analysis

The SEC-MALLS system used to determine the molecular weight of the *Pongamia* nanocellulose consisted of a guard column, SEC column, and a MALLS detector. The guard and SEC columns were KD-806M and KD-G, from Shodex, Japan. The MALLS detector used was DAWN HELEOS-II, from Wyatt Technologies, USA. The SEC sample concentration was kept at 0.1% (w/w). The injection volume was 100 µL and the flow rate was 0.5 mm/min. The column, PDA and RI detector were maintained at 40 °C, while the MALLS detector was kept at room temperature. Before the experiment, the sample solution and the eluent (1% LiCl/DMAc) were filtered through a 0.2 µm and 0.1 µm PTFE membrane, respectively. The SEC-MALLS data were analyzed using the ASTRA software.[26,27]

Fourier transform infrared studies

A Shimadzu IRAffinity-1S Fourier transform infrared spectrophotometer was used to record the spectra of the *Pongamia* nanocellulose powder. The spectra were recorded in total attenuated reflectance mode using a diamond cell. Sixty-four scans were collected in the range of 400-4000 cm^{-1}. LabSolutions Series software was used to analyze the obtained spectra.

X-ray diffraction

X-ray diffraction studies of the nanocellulose samples were performed using a Bruker AXS D8 Advance diffractometer (Mumbai, India), which had an SSD-160 detector with nickel filter for Cu Kα radiation, whose wavelength was 1.54 Å. The sample holder was made out of teflon. The diffractometer was operated at 45 kV voltage and 20 mA current, in the continuous PSD fast scan mode. XRD data were acquired in the 2 theta range from 10° to 70°. The patterns obtained were analyzed using DIFFRAC.EVA software.

Thermogravimetric analysis

The thermal behavior of *Pongamia* nanocellulose powder was studied using a thermogravimetric analyser (Mettler Toledo, Model 822e). Samples were placed in sealed aluminum pans and heated at a rate of 10 °C/min from 25 °C to 600 °C under air.

RESULTS AND DISCUSSION

Morphology studies

TEM and AFM micrographs of a very dilute suspension (0.1 mg/mL) of nanoparticles are shown in Figures 1 and 2, respectively. It can be observed that cellulose nanorods are agglomerated in a few areas, whereas they look quite separated in many other places. The distribution range of the particles was quite high and it is clear from the images that the dimensions of the particles were in the nanoscale range (less than 500 nm). Also, the average thickness of the nanocellulose measured using AFM was 2.2 ± 0.868 nm. This observation was quite consistent with the particle size analysis results obtained through dynamic light scattering experiments (338 nm). Similar morphology of the

nanocellulose from rice husk and sugarcane bagasse was observed by other researchers.[3, 4]

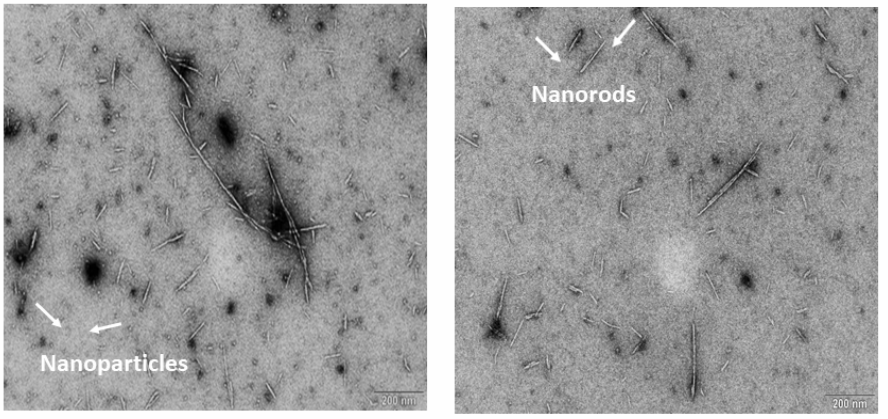


Figure 1: TEM images of obtained *Pongamia* nanorods/nanoparticles from oil meal

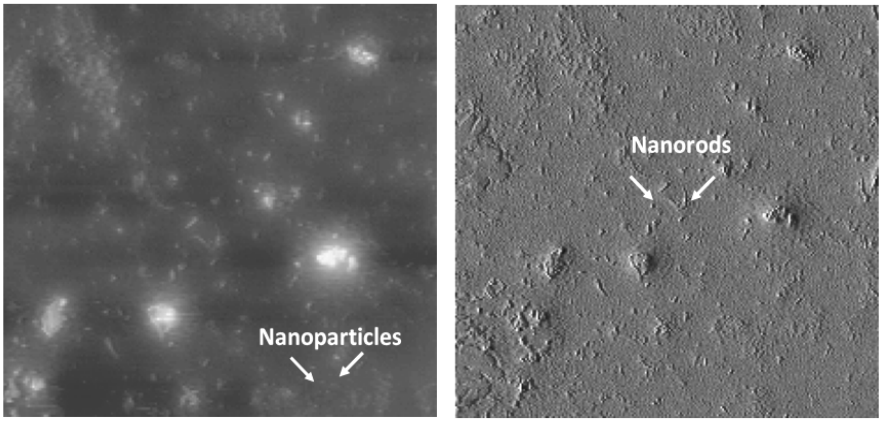


Figure 2: AFM images of *Pongamia* nanorods/nanoparticles from oil meal

Particle size and zeta potential analysis

The dynamic light scattering technique was used to find the particle size distribution of the nanofibers/nanoparticles. The statistical distribution of the nanoparticles is shown in Figure 3. It can be observed that most of the particles had dimensions in the nanoscale range. The average effective diameter of the particles was 338.8 nm. Also, it was clear that the particles were not uniformly sized and varied both in length and width.[5] This may be due to the processing conditions used for the extraction. Since most of the particles had nanoscale dimensions, it is clear that nanofibers/nanoparticles were successfully extracted.[4] A comparative report on the size of nanoparticles obtained from various sources is given in Table 1.

The mean value of the zeta potential of the cellulose nanoparticles was found to be -13.36 mV, which suggests that the particles are not stable enough and aggregate due to van der Waals interaction.[7,28] The repulsive forces between the charges on the surface of the nanoparticles and charges due to the particles present in the solution are not strong enough, hence they come together and stick to form an aggregate. Simultaneously, other particles join the growing aggregate. The aggregated particles get separated from the surrounding media and settle down.

There is a wide range of applications based on the zeta potential of nanoparticles. These include drug delivery systems,[29] water purification materials, detergents, paints, pharmaceuticals, in electrodeposition, mineral and ore flotation.[30-32] Hence, by varying the extraction and processing conditions and obtaining nanoparticles with the desired zeta potential, nanocellulose can be made suitable for various intended applications.

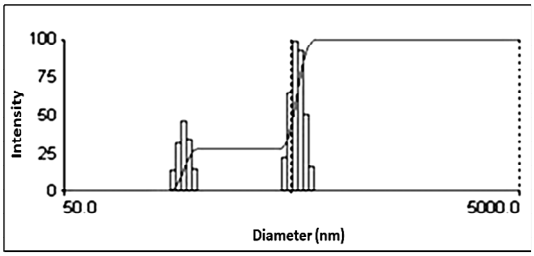


Figure 3: Size distribution of *Pongamia* nanorods/nanoparticles

Table 1
Comparison of size of nanocellulose particles obtained in previous studies from different sources

Source	Extraction method	Particle size	Reference
China cotton	Acid catalysis	30-60 nm	[8]
Rice husk	Acid and alkali catalysis	10-15 nm	[3]
Cotton linter	Acid hydrolysis	9.2 nm	[7]
Sisal fibers	Acid hydrolysis	30.9 ± 12.5 nm	[5]
Jute fibers	Ball milling	148 nm	[41]
Olive fiber	Alkaline treatment	168 nm	[42]
Palm oil biowaste	Alkaline treatment and acid hydrolysis	499.2 nm	[43]
Hemp fibers	Alkalization and acid hydrolysis	403 ± 159 nm	[44]
Palm tree fronds, leaves and coir	Alkaline treatment and acid hydrolysis	42-82 nm	[45]
Microfibrillated cellulose	Supercritical CO_2 and ethanol	200 nm length, 20 nm width	[46]
Commercial microcrystalline cellulose	Acid hydrolysis with different Lewis acids as catalysts	66-1125 nm	[47]
Pongamia oil cake	Alkali treatment, bleaching, and acid treatment	338 nm	This study

Coupled SEC and MALLS

The molecular weight distribution of *Pongamia* nanocellulose is depicted in Figure 4. The various averaged molecular weights attained are M_w = 54300, M_n = 14600, and the polydispersity value of the sample M_w/M_n was found to be 3.73. The degree of polymerization, DP_w, of the obtained nanocellulose samples was 335. Also, it is clear from the figure that the sample is broad enough to offer a range of molecular weights.[33] This can be attributed to the source and method employed for the extraction of nanocellulose. It was reported by Oberlerchner[26] that, for non-uniform samples, the weight average molecular weight, M_w, is greater than the number average molecular weight, M_n. However, for uniform samples, the values will be the same.[26] Hence, the nanocellulose extracted from *Pongamia* oil meal is non-uniform and this observation is quite consistent with the results obtained through other characterization techniques. In another study, the molecular weights of the cellulose samples obtained by the delignification of eucalyptus and Japanese cedar were 347000 and 890000, respectively. When cellulose was obtained from eucalyptus and Japanese cedar by delignification using NaOH, followed by acid hydrolysis, the molecular weights reduced to 166000 and 189800, respectively.[34] In a different study, linter cellulose was oxidized by the NaClO/NaBr/2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) system at pH 10.5, and the obtained products were studied. The weight average molecular weights of cellulose before and after oxidation were 137000 and 120000, respectively, according to SEC-MALLS analysis. Also, the degree of polymerization before and after treatment was 550 and 370, respectively.[27]

Fourier transform infrared spectroscopy

To understand the changes occurring in chemical structure during the treatments to extract the cellulose and then the nanocellulose from the *Pongamia* oil meal, Fourier transform infrared spectroscopy studies were carried out (Fig. 5).

Most notably, there was a decrease in the intensity of the peaks due to the change in the crystal structure of cellulose.[35] A drastic decrease in the intensity of the peaks of nanocellulose around 1430 cm^{-1} represents CH_2 bending vibration (crystallinity band). The reduction in the intensity of the peaks suggests that cellulose loses its crystallinity during regeneration and successive dispersion to form nanocellulose.[36,38] The peaks around 3400 cm^{-1} are due to C-H and O-H group vibrations. A small shoulder around 1700 cm^{-1} in the cellulose spectra corresponds to the acetyl or ester groups in hemicelluloses or carboxylic groups of lignin.[37] This peak disappears in the case of nanocellulose, due to the removal of non-cellulosic materials. The peak seen around 2894 cm^{-1} indicated C-H stretching in both samples. The O-H bending peak due to adsorbed water was observed around 1640 cm^{-1}. The peaks at 1150 and 1100 cm^{-1}, ascribed to the C-C ring and the C-O-C glycosidic bond from the polysaccharide component, converge to a sharper and narrower peak at 1050 cm^{-1} in nanocellulose, which can be attributed to the hydrolysis reaction and subsequent reduction in molecular weight.[4] This observation is supported by the results obtained in XRD studies.

X-ray diffraction studies

Figure 6 shows the X-ray diffraction patterns of *Pongamia* cellulose and nanocellulose. Cellulose exhibits characteristic crystalline peaks around 2 theta values of 22.6°, 14.8°, 16.2° and 34.5°, corresponding to the (200), (−110), (110) and (400) lattice planes, respectively, which are characteristic of cellulose I structure.[39] However, nanocellulose shows the characteristic crystalline peaks at 2 theta values of 12.03°, 20.19° and 22.5°, corresponding to the (110), (−110) and (200) lattice planes, respectively, which is a characteristic of cellulose II structure.[39] Hence, *Pongamia* nanocellulose had characteristics similar to those of cellulose II.

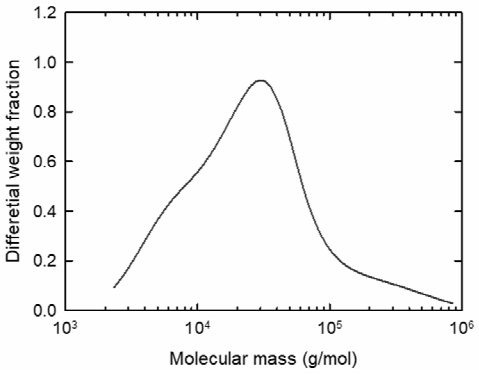


Figure 4: SEC-MALLS profile with the molecular mass of extracted *Pongamia* nanocellulose

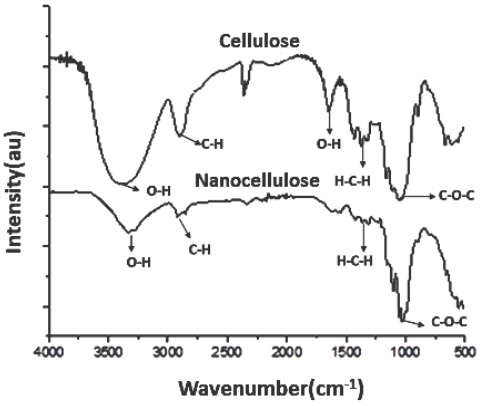


Figure 5: FTIR spectra of cellulose and nanocellulose obtained from *Pongamia* oil meal

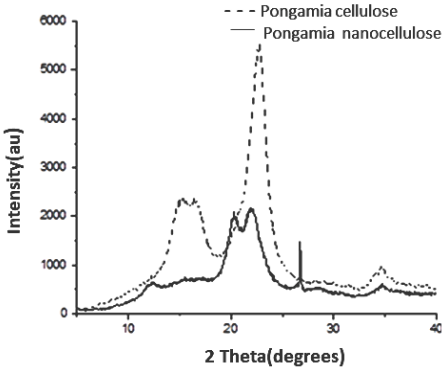


Figure 6: XRD patterns of cellulose and nanocellulose from *Pongamia* oil meal

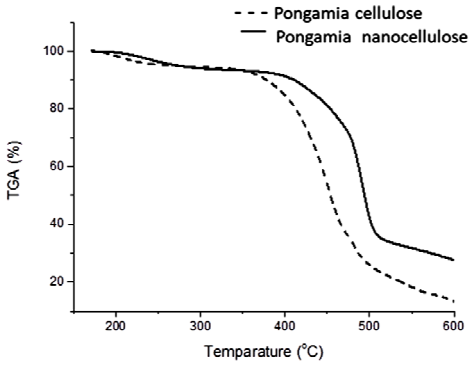


Figure 7: TGA plot of *Pongamia* cellulose and nanocellulose

The peak at the 2 theta value of 22.6° was much broader in the case of nanocellulose, in comparison with that of cellulose, indicating a reduction in the crystallinity of nanocellulose. Similar results of reduced crystallinity have been observed when cellulose was treated with high concentration (7%,w/v) of NaOH.[36,38] In another study by Mandal, the XRD peak of nanocellulose (obtained from bagasse) at a 2 theta value of 22.5° displayed a doublet similar to the ones we have obtained. The coexistence of cellulose I and cellulose II allomorphs is said to be the reason behind this.[4] The XRD peak of nanocellulose obtained from commercially available microcrystalline cellulose through alkaline treatment also displayed a broader peak at 22.6°.[36]

Thermogravimetric analysis

Both *Pongamia* cellulose and nanocellulose displayed similar degradation patterns with 2 drifts (Fig. 7). The first degradation stage was around 150 °C and the second one around 350 °C. The major change in the curves occurred around 350 °C due to the degradation of the cellulosic material.[7] It can be observed that the temperature where the major degradation occurs shifted to a higher temperature of around 410-430 °C, in the case of nanocellulose, compared to that of its corresponding raw material. Similar stability of fibrils was reported by Das *et al*.[40] and Johar[8] in nanocellulose extracted from cotton, waste tissue and rice husk.[3,8,40]

CONCLUSION

Nanocellulose, in the form of nanorods and nanoparticles, was extracted from the protein-free portion of *Pongamia pinnata* oil meal. The protein-free portion of the meal was treated in alkali, followed by bleaching and finally by acid treatment to obtain nanocellulose. TEM and AFM images proved the presence of both nanorods and nanoparticles. The average effective diameter and mean zeta potential of the nanocellulose were 338 nm and -13.3 mV, respectively, according to dynamic light scattering experiments. The weight average molecular weight and the degree of polymerization obtained by SEC-MALLS were 54300 and 335, respectively. The crystallinity of nanocellulose had reduced in comparison with that of cellulose. Thermal analysis indicated that the stability of nanocellulose was higher, compared to that of cellulose. *Pongamia* nanocellulose could be utilized for various medical and non-medical applications, based on its zeta potential values. However, further studies are required to optimize the extraction conditions to obtain favorable zeta potential and uniform morphology of the nanoparticles.

ACKNOWLEDGMENTS: The authors would like to acknowledge CIIRC, Jyothy Institute of technology, Thathaguni for their financial support.

REFERENCES

[1] K. P. Y. Shak, Y. L. Pang and S. K. Mah, *Beilstein J. Nanotechnol.*, **9**, 2479 (2018), https://doi.org/10.3762/bjnano.9.232

[2] N. Siddiqui, R. H. Mills, D. J. Gardner and D. Bousfield, *J. Adhes. Sci. Technol.*, **25**, 709 (2011), https://doi.org/10.1163/016942410X525975

[3] N. Johar, I. Ahmad and A. Dufresne, *Ind. Crop. Prod.*, **37**, 93 (2012), https://doi.org/10.1016/j.indcrop.2011.12.016

[4] A. Mandal and D. Chakrabarty, *Carbohyd. Polym.*, **86**, 1291 (2011), https://doi.org/10.1016/j.carbpol.2011.06.030

[5] J. I. Morán, V. A. Alvarez, V. P. Cyras and A. Vázquez, *Cellulose*, **15**, 149 (2008), https://doi.org/10.1007/s10570-007-9145-9

[6] Q. Liu, Y. Lu, M. Aguedo, N. Jacquet, C. Ouyang *et al*., *ACS Sust. Chem. Eng*., **5**, 6183 (2017), https://doi.org/10.1021/acssuschemeng.7b01108

[7] J. P. S. Morais, M. de Freitas Rosa, L. D. Nascimento, D. M. do Nascimento and A. R. Cassales, *Carbohyd. Polym*., **91**, 229 (2013) https://doi.org/10.1016/j.carbpol.2012.08.010

[8] S. Maiti, J. Jayaramudu, K. Das, S. M. Reddy, R. Sadiku *et al*., *Carbohyd. Polym*., **98**, 562 (2013), https://doi.org/10.1016/j.carbpol.2013.06.029

[9] G. Siqueira, J. Bras and A. Dufresne, *BioResources*, **5**, 727 (2010), https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_05_2_0727__Siqueira_BD_Luffa_lignocel_MFC_nanocryst

[10] M. Jonoobi, A. P. Mathew and K. Oksman, *Ind. Crop. Prod.*, **40**, 232 (2012), https://doi.org/10.1016/j.indcrop.2012.03.018

[11] E. Qua, P. Hornsby, H. Sharma and G. Lyons, *J. Mater. Sci*., **46**, 6029 (2011), https://doi.org/10.1007/s10853-011-5565-x

[12] S. Elazzouzi-Hafraoui, Y. Nishiyama, J.-L. Putaux, L. Heux, F. Dubreuil *et al*., *Biomacromolecules*, **9**, 57 (2008), https://doi.org/10.1021/bm700769p

[13] Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev*., **110**, 3479 (2010), https://doi.org/10.1021/cr900339w

[14] P. A. Penttilä, T. Imai, J. Hemming, S. Willför and J. Sugiyama, *Carbohyd. Polym*., **190**, 95 (2018), https://doi.org/10.1016/j.carbpol.2018.02.051

[15] P. Phanthong, P. Reubroycharoen, X. Hao, G. Xu, A. Abudula *et al*., *Carbon Res. Conv*., **1**, 32 (2018), https://doi.org/10.1016/j.crcon.2018.05.004
[16] H. Kargarzadeh, M. Ioelovich, I. Ahmad, S. Thomas and A. Dufresne, "Handbook of Nanocellulose and Cellulose Nanocomposites", vol. 1, 2017, https://onlinelibrary.wiley.com/doi/book/10.1002/9783527689972
[17] S. Janardhnan and M. M. Sain, *Bioresources*, **1**, 176 (2006), https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_01_2_176_188_Janardnan_Sain_Isoluation_Cellulose_Microfibrils_Enzymatic
[18] D. Klemm, B. Heublein, H. P. Fink and A. Bohn, *Angew. Chem. Int. Ed*., **44**, 3358 (2005), https://doi.org/10.1002/anie.200460587
[19] L. Heux, G. Chauve and C. Bonini, *Langmuir*, **16**, 8210 (2000), https://doi.org/10.1021/la9913957
[20] E. C. Lengowski, E. A. B. Júnior, M. M. N. Kumode, M. E. Carneiro and K. G. Satyanarayana, in "Sustainable Polymer Composites and Nanocomposites", Springer, 2019, pp. 1027-1066, https://link.springer.com/book/10.1007/978-3-030-05399-4
[21] C. Guise and R. Fangueiro, in "Natural Fibres: Advances in Science and Technology towards Industrial Applications", Springer, 2016, pp. 155-169, https://link.springer.com/book/10.1007/978-94-017-7515-1
[22] R. Mu, X. Hong, Y. Ni, Y. Li, J. Pang *et al*., *Trends Food Sci. Technol*., **93**, 136 (2019), https://doi.org/10.1016/j.tifs.2019.09.013
[23] P. T. Scott, L. Pregelj, N. Chen, J. S. Hadler, M. A. Djordjevic *et al*., *Bioenerg. Res*., **1**, 2 (2008), https://doi.org/10.1007/s12155-008-9003-0
[24] S. H. Gorissen, J. J. Crombag, J. M. Senden, W. H. Waterval, J. Bierau *et al*., *Amino Acids*, **50**, 1685 (2018), https://doi.org/10.1007/s00726-018-2640-5
[25] C. Hu, D. Nataraj and N. Reddy, *J. Polym. Environ*., **26**, 1371 (2018), https://doi.org/10.1007/s10924-017-1034-1
[26] J. T. Oberlerchner, T. Rosenau and A. Potthast, *Molecules*, **20**, 10313 (2015), https://doi.org/10.3390/molecules200610313
[27] T. Saito, M. Yanagisawa and A. Isogai, *Cellulose*, **12**, 305 (2005), https://doi.org/10.1007/s10570-004-5835-8
[28] H. Mirhosseini, C. P. Tan, N. S. Hamid and S. Yusof, *Coll. Surf. A*: *Phys. Eng*., **315**, 47 (2008), https://doi.org/10.1016/j.colsurfa.2007.07.007
[29] S. Honary and F. Zahir, *Trop. J. Pharm. Res*., **12**, 255 (2013)
[30] B. B. Weiner, W. Walther and D. F. Tscharnuter, *Procs. Canadian Mineral Analysts Meeting*, (1993), http://www.brookhaven.de/data/Weiner_Zeta_Pot.pdf
[31] C. Jacobs, O. Kayser and R. Müller, *Int. J. Pharm*., **196**, 161 (2000), https://doi.org/10.1016/S0378-5173(99)00412-3
[32] K. Ofokansi, G. Winter, G. Fricker and C. Coester, *Eur. J. Pharm. Biopharm*., **76**, 1 (2010), https://doi.org/10.1016/j.ejpb.2010.04.008
[33] M. P. Tarazona and E. Saiz, *J. Biochem. Biophys. Methods*, **56**, 95 (2003), https://doi.org/10.1016/S0165-022X(03)00075-7
[34] Y. Ono, R. Funahashi, T. Saito and A. Isogai, *Cellulose*, **25**, 2667 (2018), https://doi.org/10.1007/s10570-018-1713-7
[35] M. Adsul, S. K. Soni, S. K. Bhargava and V. Bansal, *Biomacromolecules*, **13**, 2890 (2012), https://doi.org/10.1021/bm3009022
[36] S. Shankar and J.-W. Rhim, *Carbohyd. Polym*., **135**, 18 (2016), https://doi.org/10.1016/j.carbpol.2015.08.082
[37] A. Alemdar and M. Sain, *Bioresour. Technol*., **99**, 1664 (2008), https://doi.org/10.1016/j.biortech.2007.04.029
[38] A. Mittal, R. Katahira, M. E. Himmel and D. K. Johnson, *Biotechnol. Biofuels*., **4**, 41 (2011), https://doi.org/10.1186/1754-6834-4-41
[39] H. Yu, C. Yan, X. Lei, Z. Qin and J. Yao, *Mater. Lett*., **131**, 12 (2014), https://doi.org/10.1016/j.matlet.2014.05.159
[40] K. Das, D. Ray, N. Bandyopadhyay and S. Sengupta, *J. Polym. Environ*., **18**, 355 (2010), https://doi.org/10.1007/s10924-010-0167-2
[41] M. R. K. Sofla, R. J. Brown, T. Tsuzuki and T. J. Rainey, *Adv. Nat. Sci.*: *Nanosci. Nanotechnol*., **7**, 035004 (2016), https://iopscience.iop.org/article/10.1088/2043-6262/7/3/035004/meta
[42] L. Kian, N. Saba, M. Jawaid, O. Alothman and H. Fouad, *Carbohyd. Polym*., **241**, 116423 (2020), https://doi.org/10.1016/j.carbpol.2020.116423
[43] B. Shanmugarajah, P. L. Kiew, I. M. L. Chew, T. S. Y. Choong and K. W. Tan, *Chem. Eng. Trans*., **45**, 1705 (2015), https://doi.org/10.3303/CET1545285
[44] G. Mondragon, S. Fernandes, A. Retegi, C. Peña, I. Algar *et al*., *Ind. Crop. Prod*., **55**, 140 (2014), https://doi.org/10.1016/j.indcrop.2014.02.014.
[45] S. Mehanny, E. E. Abu-El Magd, M. Ibrahim, M. Farag, R. Gil-San-Millan *et al*., *J. Mater. Res. Technol*., **10**, 526 (2021), https://doi.org/10.1016/j.jmrt.2020.12.027
[46] Z. Hu, X. Cao, D. Guo, Y. Xu, P. Wu *et al*., *Cellulose Chem. Technol*., **55**, 501 (2021), https://doi.org/10.35812/CelluloseChemTechnol.2021.55.45
[47] C. T. M. Kishimoto, L. Moerschbacher, R. A. Prestes, J. C. Hoepfner and L. A. Pinheiro, *J. Nanoparticle Res*., **22** (2020), https://doi.org/10.1007/s11051-020-04928-1