# Preparation and Characterisation of Cellulose Nanocrystal from Sugarcane Peels by XRD, SEM and CP/MAS $^{13}$C NMR

IOP Conf. Series: Journal of Physics: Conf. Series **1299** (2019) 012123 doi:10.1088/1742-6596/1299/1/012123

# Preparation and Characterisation of Cellulose Nanocrystal from Sugarcane Peels by XRD, SEM and CP/MAS $^{13}$C NMR

**Chioma Vivian Abiaziem[1,2*], Akan Bassey Williams[1], Adedayo Ibijoke Inegbenebor[1], Chionyedua Theresa Onwordi[3,4], Cyril Osereme Ehi-Eromosele[1], Leslie Felicia Petrik[3]**

Department of Chemistry, Covenant University, Km 10, Canaan Land, Ota, P.M.B 1023, Ota, Ogun State, Nigeria

[2]Science Laboratory Technology Department, The Federal Polytechnic Ilaro, P.M.B 50, Ilaro, Ogun State, Nigeria

[3]Department of Chemistry, Environmental and Nano Sciences Group, University of the Western Cape, Bellville, Cape Town, 7535, South Africa

[4]Department of Chemistry, Lagos State University, Ojo, LASU P.O.Box 0001, Ojo, Lagos State, Nigeria

*Corresponding author E-mail: vyvycox@yahoo.com

**Abstract.** Sugarcane peels are agro-waste resources discarded before taking the sugarcane juice. In the present study, cellulose nanocrystal was isolated from sugarcane peel by sulphuric acid hydrolysis. Two pretreatments, alkaline treatment and bleaching with acidified sodium chlorite, were applied. Sulphuric acid hydrolysis was performed at 45$^0$C for 45 min using 64% concentrated sulphuric acid. The resulting cellulose nanocrystal (CNC) of the sugarcane peel was characterised by studying the surface morphology using scanning electron microscope (SEM). X-ray diffraction (XRD) was studied to identify the crystalline nature of the CNC. CP/MAS $^{13}$C solid- state NMR was used to evaluate the purity and molecular structure of the CNC. The SEM image of the nanocrystal showed that the bundles of fibre were separated into individual CNC, with the size decreasing to a nanosize indicating an effective removal of the amorphous region. XRD diffraction pattern showed that the CNC possessed the cellulose crystalline configuration with crystallinity index of 99.2% and crystallite particle size dimension of 5.56 nm. The NMR spectra of the CNC revealed that all the signals have six carbon atoms of cellulose and the disappearance of several signals also indicated the disruption of the amorphous region. The results revealed effective synthesis of CNC from sugarcane peel, suggesting the leaching of the amorphous domain, apparent crystallinity and purity of the CNC. The cellulose nanocrystal prepared is considered to be a potent material for various industrial applications.

**Keywords:** Sugarcane peel, cellulose nanocrystal, SEM, XRD, CP/MAS $^{13}$C NMR, agricultural waste

## 1. Introduction

Over the last few decades, there has been a fast growth in the development of nanotechnology from cellulose materials. Cellulose which is an abundant polymer has attracted considerable attention in various uses in areas such as bio-composite, medicine, treatment of water, food packaging, reinforcement,etc [1][2]. Moreover, it is a renewable, biocompatible and biodegradable organic polymer, identified as an alternative to non-degradable fossil fuel-based polymers [3].

Cellulose nanocrystal (CNC) prepared from hydrolysis of sulphuric acid from cellulose fibres, has been found as a new group of nanomaterial's. Likened to cellulose fibres, cellulose nanocrystal has several advantages, such as reduced toxicity, nanoscale size, high surface area, etc. [4][5]. The synthesis of cellulose nanocrystals from cellulosic fibres often consists of an acid destructive method, including penetration of acid unit into cellulose fibres and glycosidic bonds cleavage. Numerous concentrated acids such as hydrobromic, sulphuric, phosphoric, hydrochloric, nitric acids and a combination of hydrochloric and organic acids are effectively used to extract crystalline cellulosic nanoparticles [5]. Sulphuric acid ($H_2SO_4$) is commonly used for nanocellulose preparation via acid hydrolysis. This study targets at isolating cellulose nanocrystal from a renewable, low cost, sustainable and unused source fibre; sugarcane peel. The resultant nanocrystal was characterised by SEM, XRD and NMR. The morphology of the sample was determined using the SEM instrument. XRD was used to identify the crystallinity of the material while the NMR was used to evaluate the purity and molecular structure of the compounds. These techniques were used to investigate the potential use of the cellulose nanocrystal isolated from sugarcane peel with a view to using them for various industrial uses.

## 2. Materials and Methods

### *2.1. Materials*

Sugarcane peels used in this study were collected from different sugar cane farms at Papalanto and Sagamu areas in Ogun State, Nigeria. The chemicals used were: acetic acid, toluene, sodium chlorite, ethanol, sodium hydroxide, and sulphuric acid. All the chemical used were of analytical grade and procured from Sigma Aldrich and Merck South Africa.

### *2.2 Isolation of Purified Cellulose (PC)*

The sample was air-dried for several days, milled and sieved with a 30 mesh sieve. The sample was preserved at 25$^{o}$C in a tight polyethylene bag. Purified cellulose from sugarcane peel (SP) was isolated as earlier reported with minor modifications by [6][7][8][9]. The sugarcane peel sample (30 g) was extracted with toluene and ethanol mixture of 2:1v/v for 6 h to remove wax and oil and dried at 60°C.The dewaxed sample was saturated in 50 g/L of 5% sodium hydroxide solution at 25$^{o}$C for 24 h and heated at 90$^{o}$C for 2 h. This was cleaned with distilled water until neutral pH, then oven-dried at 50$^{o}$C for 16 h. The residual alkaline treated sample was then delignified using 2.5 % w/v of acidified sodium chlorite using material to solution of 1:20 for 4 h at 100$^{o}$C. The delignified cellulose was, thereafter, rinsed to neutral pH and oven-dried at 50$^{o}$C for 16. Finally, the product (chemically purified cellulose) was stored properly for characterisation.

### *2.3 Synthesis of Cellulose Nanocrystals*

Chemically purified cellulose produced from peel of sugarcane was synthesised into cellulose nanocrystal (CNC) by acid-hydrolysis, according to the method adopted by [10][7]. The cellulose isolated from sugarcane peel was hydrolysed with 64 wt.% sulphuric acid at 10 mL/g at a temperature of 45$^{o}$C for 45 min with vigorous mechanical stirring. Reaction of hydrolysis was quenched with 10-times cold water. The resultant CNC gel was centrifuged at 45000 rpm for 30 min to concentrate the cellulose nanocrystal; the filtrate was then decanted. The resultant precipitate was dialysed with cellulose dialysis tube (Sigma –Aldrich, South Africa) against ultra-pure water until attaining neutral pH (pH 6-7). The suspension was

sonicated at an amplitude of 40% in an ice bath to disrupt solid aggregates and avoid overheating. The resultant CNC suspension was freeze-dried (–47$^{o}$C, 0.2 mbar). The dried sample was stored in an air tight container for characterisation. Figure 1 shows the schematic illustration of the production of cellulose nanocrystal from sugarcane peel.


**Figure 1:** Schematic representation of the preparation of cellulose nanocrystal from sugarcane peel.

*2.4. Characterisation*

*2.4.1. X-ray Diffraction (XRD) Spectroscopy*

X-ray diffraction was carried out using Philips X-pert MPD X-ray diffractometer with Cu-K radiation operating at 40 kV and 40 Ma, to identify the crystallinity nature of the material. The sample was scanned over a range of 5$^{o}$ to 70$^{o}$ at 2θ with the count step size programmed at 0.5 seconds per step/0.05 step size. The maximum intensity of the principle peak of 200 ($I_{002}$, 2θ= 22°) was calculated from the crystallinity index (CI) and the intensity of diffraction of 110 peaks ($I_{am}$, 2θ=16°) using the Seagal method [11][12].

$I_{002}$ denote crystalline and Iam denotes the amorphous material.

$$CI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

*2.4.2. High Resolution Scanning Electron Microscopy (HRSEM)*

AURIGA Field Emission HRSEM was used to analyse the superficial morphology of the raw, treated and the nanocrystal. The samples were prepared by coating with carbon to make SEM analysis conductive. The HRSEM sample images were taken at diverse magnification.

*2.4.3. Nuclear Magnetic Resonance (NMR) Spectroscopy*

The NMR spectroscopy is a technique used to evaluate the purity and molecular structure of compounds. In this study, the carbon group was examined using solid NMR technique. For

solid NMR, 20 mg of nanocrystals was dissolved in 500 µL in DMSO- $d_6$ solvent in an NMR tube. The $^{13}C$ CPMAS spectra were recorded on an 11.4 Tesla Bruker Avance III HD NMR spectrometer, working at frequencies of 500 MHz (1H) and 125 MHz ($^{13}C$).

## 3. Results and Discussion

### *3.1. X-ray Diffraction Analysis*

Figure 2 presents the XRD graph of sugarcane peel (RSP, SPCPC and SPCNC). The characteristic peak of SP identified at 2θ=16.89°, and 34.70° of 110 and 400 lattice planes of cellulose I, indicates the occurrence of the amorphous region. Also, the peak at 2θ=16.71° of the lattice plane of 110 for the SPCPC and the disappearance of the peak at the lattice plane of 400 indicates the partial removal of the amorphous region. The disappearance of the peaks at 110 and 400 lattice planes for the SPCNC, indicates a complete removal of the amorphous domain. The peak at 2θ value of 22.47° shows the crystallinity configuration of cellulose [7]. The crystallinity index of SP, SPCPC and SPCNC was calculated to be 86.5%, 95.6%, and 99.2% with a particle size of 5.56 nm, 21.1 nm and 25.7 nm respectively. The benefits of having increased crystallinity index >70% comprise of the important increase of bacteria resistance, chemical and thermal stability [13]. The crystallinity index increased progressively from the raw to the CNC, similar to the result obtained by [14][7].

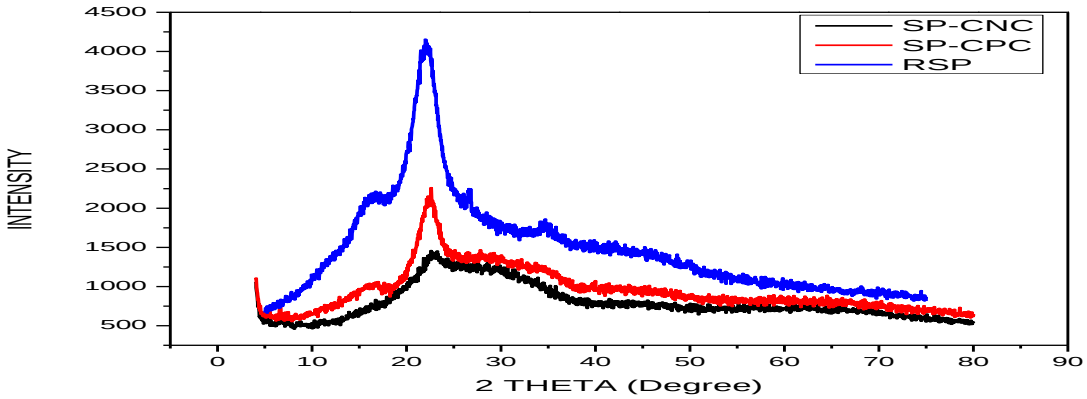


**Figure 2:** X-ray diffraction patterns of (a) Raw sugarcane peel (RSP) (b) Cellulose (SPCPC) (c) Cellulose nanocrystal (SPCNC).

### *3.2. Scanning Electron Microscopy (SEM) Analysis*

The smooth surface of the untreated sample of the sugarcane peel is attributed to the availability of some non-cellulose constituents in the surface of the fibre such as lignin, hemicellulose, wax, oil etc. (Figure 3a). On subsequent treatment with alkaline and delignification with acidified sodium chlorite, it was evident that lignin and hemicellulose were removed as revealed by [15][16].

The alkaline treatment revealed that the hemicellulose became water soluble after been hydrolysed, the fibrils were defibrillated as shown in Figure 3b. After the chemical treatment of the raw fibre, a narrow fibril and reticular structure of the fibre which is the chemically purified cellulose was seen, indicating that the procedure of alkaline treatment and delignification did not completely disrupt the cellulose structure and remove the amorphous region. The surface morphology of the raw samples was different from that of the SPCPC

with a decrease in size which may have ensued from the disruption of the amorphous domain [17]. The features of the cellulose nanocrystal in the sugarcane peel, showed that there was a reduction in the fibrillar structure size and intermittent breakdown in fibrillar structure into individualised fibrils. Figure 3c and 3d represent the freeze-dried cellulose nanocrystal, the configuration of the cellulose was absolutely shattered and the dimension was considerably reduced to nanosize as pointed out by [18].

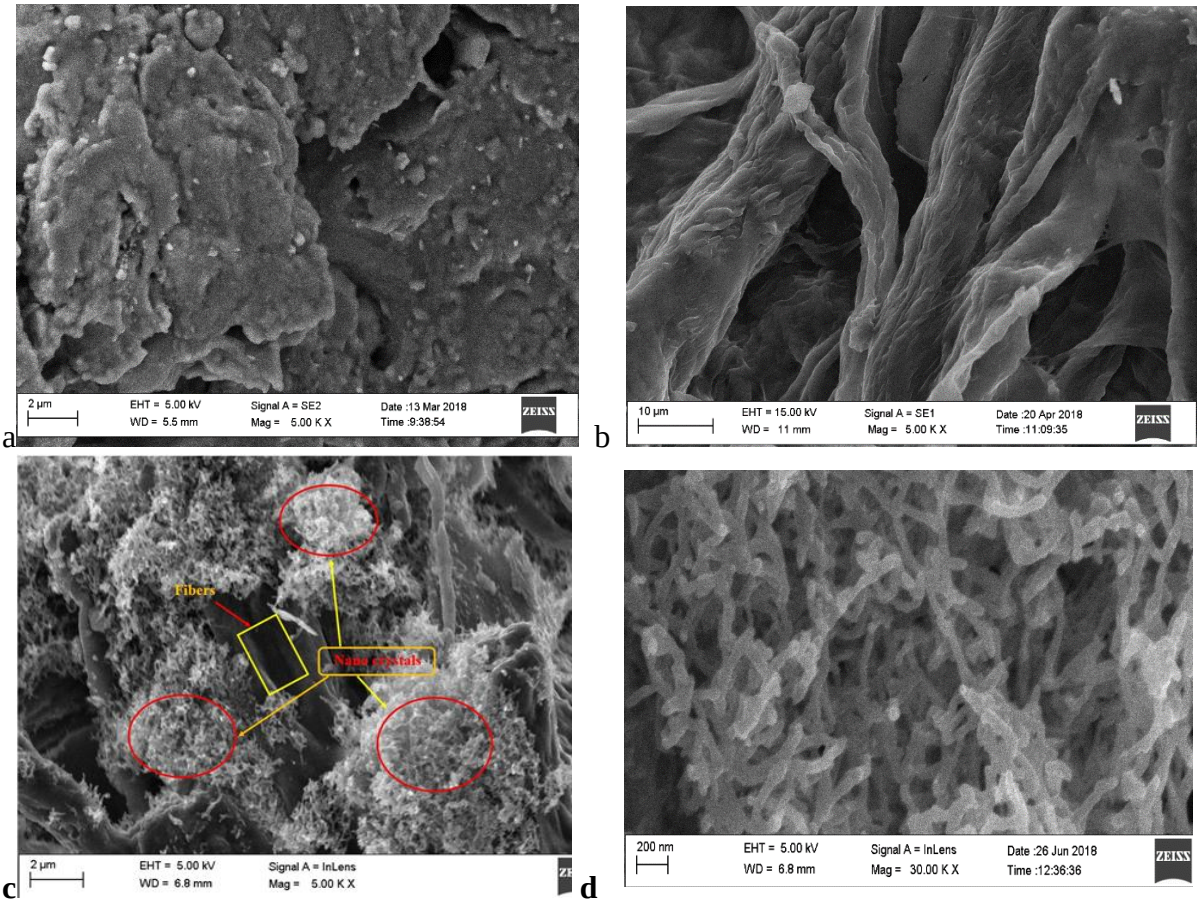


**Figure 3:**SEM images of the (a) raw sample, (b) cellulose and (c,d) nanocrystal of sugarcane peel

*3.3. CP/MAS 13C NMR Spectra*

In summary, signals in the region between 60-110 ppm are from cellulose carbon [19]. Figure 4 shows the spectrum of cellulose nanocrystal of sugarcane peel, the peak 105.5 ppm relates to C1 of cellulose, 89.3 is attributed to C4 of crystalline cellulose, 75.5 ppm corresponds to C5 of cellulose and 73.4 and 72.6 ppm relates to C2/C3 of cellulose, respectively. The peak at 65.7 ppm relates to C6 of crystalline cellulose [20][21][22].

It is clear from the NMR spectra of the SPCNC that majority of the carbohydrates were taken off during treatment with the acid. The peak at 102 ppm apportioned to hemicellulose disappeared during the treatment with acid indicating elimination of hemicellulose [20]. The absence of peak at 84 ppm of C4 of non-crystalline cellulose indicates the thorough interference of the cellulose amorphous structure during sulphuric acid

hydrolysis of both sugarcane and cassava peel [22]. The absence of peaks at 21, 56 and 173 ppm assigned to the carbon present in the methyl group, methoxyl group in lignin and carbon present in the carboxylic group indicates that treatment with sodium hydroxide considerably removed the side chain from hemicellulose and xylans [19]. Conclusively, the spectra of the SPCNC revealed that the entire peaks were due to six carbon atoms of cellulose.

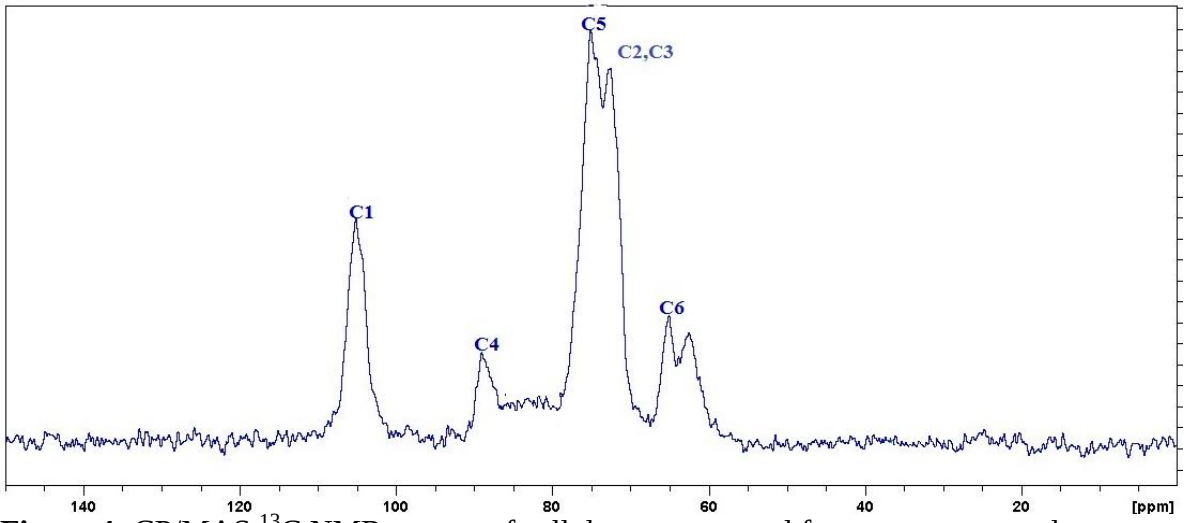


**Figure 4:** CP/MAS $^{13}$C NMR spectra of cellulose nanocrystal from sugarcane peel.

## 4. Conclusion

The present study reveals that cellulose nanocrystal was effectively prepared from sugarcane peel, proving the usage of sugarcane peel as novel fibre for the fabrication of CNC. The sulphuric acid hydrolysis conditions used led to preparing a stable nanostructured crystals from sugarcane peel. The characterisation of CNC which included morphological, crystallinity and molecular structure were investigated. The SEM image of the nanocrystal showed that the bundles of fibre were separated into discrete CNC; with the size decreasing from the untreated to the cellulose nanocrystals into a nanosize, indicating an effective removal of the amorphous region. XRD diffraction pattern showed that the CNC retained the cellulose crystalline structure with crystallinity index from raw to CNC as 86.5, 95.6 and 99.2% respectively and crystallite particle size dimension of 25.8, 21.1 and 5.56 nm from raw to CNC respectively. The NMR spectra of the CNC revealed that all the signals were attributed to six carbon atoms of cellulose and the disappearance of several signals also indicated the disruption of the amorphous region. The results revealed effective synthesis of CNC from sugarcane peel (a waste material from agricultural process). Hence, suggesting the leaching of the amorphous domain, apparent crystallinity and purity of the CNC. The cellulose nanocrystal prepared is considered to be a potent material for various industrial applications.

## Acknowledgements

The authors sincerely appreciate the financial contributions of TETFUND (Nigeria), through The Federal Polytechnic Ilaro, NRF/RISA (South Africa); NMR facility, University of the Western Cape and the support of the research laboratory of Environmental and Nano Science

Group, Chemistry Department, University of the Western Cape, Cape Town, South Africa for providing laboratory space for our research.

## References

[1] Sheltami, R. M., Abdullah, I., Ahmad, I., Dufresne, A. and Kargarzadeh, H. (2012). Extraction of cellulose nanocrystals from mengkuang leaves (*Pandanus tectorius*). *Carbohydrate Polymers,* 88(2), 772-779. http://dx.doi.org/10.1016/j.carbpol.2012. 01.062.

[2] Julie, C.C.S., Neena, G. and Sunil, K. N. (2016). Isolation and characterization of cellulose nanofibrils from arecanut,husk fibre. *Carbohydrate Polymers*, 142, 158-166.

[3] Johnsy, G. and Sabapathi, S. N. (2015). Cellulose Nanocyrstals: synthesis, functional properties and applications. *Nanotechnology Science and Application,* 8, 45-54.

[4] Ng, H. M., Sin, L. T., Tee, T. T., Bee, S. T., Hui, D., Low, C. Y. and Rahmat, A. R. (2015). Extraction of cellulose nanocrystals from plant sources for application as reinforcing agent in polymers. *Composites Part B: Engineering,* 75, 176–200. http://dx.doi.org/10. 1016/j.compositesb.2015.01.008.

[5] Habibi, Y., Lucia, L. and Rojas, O. J. (2010). Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chemical Reviews,* 110, 3479-3500. http://dx.doi.org//:10.1021/cr900339w.

[6] Lu, P. and Hsieh, Y. (2012). Preparation and characterization of cellulose nanocrystals from rice straw. *Carbohydrate Polymers*, 87, 564– 573.

[7] Rahimi, M. K. S., Brown, R. J., Tsuzuki, T. and Rainey, T. J. (2016). A comparison of cellulose nanocrystals and cellulose nanofibres extracted from bagasse using acid and ball milling methods. *Advances in Natural Sciences: Nanoscience and Nanotechnology,* 7, 1-9. http://dx.doi.org//:10.1088/2043-6262/7/3/035004

[8] Shaheen, T. I. and Emam, H. E. (2018). Sono-chemical synthesis of cellulose nanocrystals from wood sawdust using Acid hydrolysis. *International Journal of Biological Macromolecules*, 107, 1599-1606.

[9] Anuj, K., Yuvraj, S. N., Veena, C. and Nishi, K. B. (2014). Characterization of cellulose nanocrystals produced by acid-hydrolysis from sugarcane bagasse as agro-waste. *Journal of Materials Physics and Chemistry,* 2(1), 1-8.

[10] Naduparambath, S., Jinitha, T. V., Shaniba, V., Sreejith, M. P., Aparna, K. B, and Purushothaman, E. (2018). Isolation and characterisation of cellulose nanocrystals from sago seed shells. *Carbohydrate Polymers,* 180, 13–20.

[11] Azubuike, C. P., Rodríguez, H., Okhamafe, A. O. and Rogers, R. D. (2012). Physicochemical properties of maize cob cellulose powders reconstituted from ionic liquid solution. *Cellulose,* 19(2), 425–433.

[12] Seagal, L., Creely, J. J., Martin, A. E. and Conrad, C. M. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using X-ray diffractometer. *Textile Research Journal,* 29, 786-794.

[13] Mohammad, M. A., Salleh, W. N. W., Jaafar, J., Ismail, A.F., Mutalib, M. A., Mohamad, A. B., Zaind, M. F. M., Awangb, N. A. and Mohd Hir, Z. A. (2017). Physicochemical characterization of cellulose nanocrystal andnanoporous self-assembled CNC membrane derived from Ceibapentandra. *Carbohydrate Polymers,* 157, 1892-1902.

[14] Nurain J., Ishak A., Alain, D. (2012). Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk. *Industrial Crops and Products*, 37, 93– 99.

[15] Ilyas, R. A., Sapuan, S. M., Ishak, M. R. (2018). Isolation and characterization of nanocrystalline cellulose from sugar palm fibres (Arenga Pinnata). *Carbohydrate Polymers,* 181, 1038-1051.

[16] Arup, M., Debabrata, C. (2011). Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. *Carbohydrate Polymers*, 86:1291-1299.

[17] Adewuyi, A. and Vargas, P. F. (2016). Chemical Modification of Cellulose Isolated from Underutilized Hibiscus sabdariffa via Surface Grafting: A Potential Bio-based Resource for Industrial Application. *Kem. Ind.,* 66(7-8), 327-338.

[18] Hongjia, L., Yu, G., Longhui, Z. and Xiong, L. (2013). Morphological, crystalline, thermal and physicochemical properties of cellulose nanocrystals obtained from sweet potato residue. *Journal of Food Research International,* 50, 121-128.

[19] Wikberg, H. and Maunu, S. L. (2004). Characterisation of thermally modified hard- and softwoods by 13C CPMAS NMR. *Carbohydrate Polymers,* 58, 461-466.

[20] Idström, A., Schantz, S., Sundberg, J., Chmelka, B. F., Paul Gatenholm, P. and Nordstierna, L. (2016). 13C NMR assignments of regenerated cellulose from solid-state 2D NMR spectroscopy. *Carbohydrate Polymers,* 151, 480-487.

[21] Yu, X., Tong, S., Ge, M., Wu, L., Zuo, J., Cao, C. and Song, W. (2013). Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals. *Journal of Environmental Sciences,* 25, 933-943.

[22] Liu, C., Ren, J., Xu, F., Liu, J., Sun, J. and Sun, R. (2006). Isolation and Characterization of Cellulose Obtained from Ultrasonic Irradiated Sugarcane Bagasse. *Journal of Agricultural and Food Chemistry,* 54, 5742-5748.