IJNRD.ORG ISSN : 2456-4184
INTERNATIONAL JOURNAL OF NOVEL RESEARCH AND DEVELOPMENT (IJNRD) | IJNRD.ORG
An International Open Access, Peer-reviewed, Refereed Journal

EXTRACTION AND CHARACTERIZATION OF NANOCRYSTALLINE CELLULOSE FROM SUGARCANE BAGASSE

Ufuoma Abigail Oyohwose[1], Victoria Ikpemhinoghena Omoko[2]

[1]Department of Chemistry, College of Science, Federal University of Petroleum Resources, FUPRE, Effurun, Nigeria.

[2]Department of Chemistry, Faculty of Sciences, Delta State University, Abraka, Nigeria.

ABSTRACT: This study examined the extraction and characterization of nanocrystalline cellulose (NCC) from sugarcane bagasse (SCB) using sulphuric acid hydrolysis. The sugarcane bagasse was initially pre-treated with 4% NaOH solution to dissolve hemicelluloses, lignin, and other impurities and to isolate the cellulose. This was followed by bleaching with 5% hydrogen peroxide. The isolated cellulose was then hydrolyzed with 64% sulphuric acid to extract the nanocellulose. The crystallinity index, morphology, and structural properties of the cellulose and nanocellulose were carried out using X-ray diffractometer (XRD), scanning electron microscope (SEM) and Fourier Transform Infra-red spectroscopy (FT-IR) respectively. The crystallinity index of sugarcane, extracted cellulose, and NCC were calculated to be 58.9%, 70.4%, and 77.1% respectively. SEM analysis showed agglomerated rod-like NCC. The FT-IR results clearly showed the removal of hemicelluloses and lignin from sugarcane bagasse after pre-treatment and also confirms bonds characteristic of the functional group of pure cellulose at 3330 cm^{-1}, 2920 cm^{-1}, 1630 cm^{-1} and 896 cm^{-1}. The FT-IR results also showed that no chemical reactions resulting in changes in functional groups occurred. These results show that sugarcane bagasse of no economic value can be used in the synthesis of crystalline nanaocellulose of high industrial potentials.

Keywords: nanocrystalline cellulose, sugarcane bagasse, cellulose, acid hydrolysis.

1.0 INTRODUCTION

Plant cellulose comprises of crystalline and amorphous region in varying proportions The current demand for green chemistry, more environmentally friendly resources, and renewable raw material, has made cellulose a highly attractive and sought for material. This can be attributed to its desirable properties such as renewability, biodegradability, and non-toxicity. Cellulose is the most abundant natural polymer and it is the main constituent of plant cell walls that gives it strength and rigidity. It was first isolated from plant by Anselm Payen, a French scientist in 1838, who later determined its chemical composition [1]. It is a linear homopolymer consisting of D-anhydroglucopyranose units linked together by a β(1,4) glycosidic bonds. Cellulose can be derived from a variety of sources such as plants, microbes, and some sea animals. These include seed fibers (cotton), wood fibers (hardwoods and softwoods), bast fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo) algae (Valonica ventricosa), bacteria (Acetobacter xylinum) and sea animals (Tunicates).

Recently, nanocellulose has received a lot of attention due to its unique mechanical properties making them suitable as reinforcement in polymer nano-composites as well as rheological properties which makes them capable of influencing flow properties of liquids with which they are mixed. It has gained many applications in the field of medicine such as biomaterial for constructing tissues, tissue regeneration, tissue repair, bio-sensing, drug delivery, bio-catalysts etc. [2-4]. It has also been applied as wood adhesives [5-6], adsorption and filtration in water treatment [7], and for dye removal [8]. There are two general classes of cellulose nanomaterials that can be extracted from different sources which include: cellulose nanocrystals (CNCs) or nano-crystalline cellulose (NCC) and cellulose nanofibrils (CNFs) [9-10]. NCCs are nanometer size range in all dimensions. They are typically rod-shaped with 10-100 nm in length and 1-100 nm in diameter [11], and 54-88% crystallinity index [12], depending on the plant species, which explains why chemical compositions and dimensions of NCC materials depend largely on particular plants, their origin, and extraction methods [13-14]. A series of nanocrystalline products have been produced from various sources such as wood [15], cotton [16-18], sisal [19-20], tunicate [21-22], bacteria [23], Ramie [24].

Among the methods used in preparing NCC, acid hydrolysis method is the most commonly used method. This method occurs in two stages [25-28]. The first stage is a pre-treatment stage which involves delignification of the source material to remove hemicelluloses, lignin and other impurities, and the isolation of the cellulose fibers. The second stage is a controlled acid hydrolysis treatment to remove the amorphous region of the cellulose polymer. Natural cellulose consists of crystalline and amorphous regions. The amorphous region has lower density compared to the crystalline region [28] and so when cellulose fibers are subjected to acid treatment, the amorphous region breaks up, releasing the crystalline region.

Sugarcane bagasse is an abundantly available agro-waste worldwide and is utilized as a source of cellulose. It is the fibrous residue remaining after sugarcane stalk has been crushed and the juice extracted. Sugarcane bagasse comprises about 30-40% pith fiber and is mainly parenchyma material and bast, rind or stem fiber which is largely derived from sclerenchyma material. The fiber of sugarcane bagasse is lignocellulosic and consist of 43.8% cellulose, 28.6% hemicelluloses 23.5% lignin, 1.3% ash, and 1.3% of other components [29]. Although many lignocellulsic materials maybe used to produce nanocellulose, there is an important commercial economic advantage in using bagasse as a lignocellulosic fiber resource such as it being cheap, abundant, and non-toxic.

The aim of this study was to extract nanocrystalline cellulose (NCC) and to characterize the NCC produced using Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), and X-ray Diffractometer (XRD).

2.0. MATERIALS AND METHODS

2.1. MATERIALS

Sugarcane stalks were obtained from a farmland at Otor – Udu in Udu L.G.A. of Delta – State, Nigeria. The reagents used were sodium hydroxide, NaOH; hydrogen peroxide, H_2O_2, sulphuric acid. H_2SO_4, and sodium bicarbonate, $NaHCO_3$ and were all of analytical grade. Distilled water was used throughout the experiment.

2.2 METHODS

2.2.1. Preparation of bagasse

Sugarcane bagasse was obtained from sugarcane stalk by extracting the juice from the stalk and the bagasse dried and then ground to powder.

2.2.2. Isolation of cellulose

About 30g of the ground bagasse was treated with 200 mL of 4% NaOH for 2hrs at a temperature of 75ºC with constant stirring. The lignin and other impurities were dissolved during this treatment. This was followed by washing with distilled water. The process was repeated for the second time and then finally washed. Method used as reported by [25].

2.2.3. Bleaching treatment

The cellulose was treated with 200 mL 5% H_2O_2 solution for 1hr at a temperature of 75ºC with constant stirring. The process was repeated to achieve satisfactory bleaching. The cellulose was then washed with distilled water and dried.

2.2.4. Extraction of NCC

The purified cellulose was hydrolyzed with 64% sulphuric acid at material to liquor ratio of 1:10 for 45mins in a water bath at a constant temperature of 55ºC with constant stirring. Hydrolysis was stopped by pouring content of the beaker into a tenfold of water with stirring and then allowed to settle for about 1hr. The clear top was decanted and the content washed repeatedly with more distilled water by centrifugation at 6000rpm for 30mins. It was then washed with a solution of 5% sodium bicarbonate to neutralize residual acid. It was oven dried at 50ºC until a steady weight was obtained. Acid hydrolysis method as reported by [30] was adopted.

2.2.5 Determination of percentage yield of cellulose

The percent yield of cellulose was determined using the formula in equation 1 below.

$$\% \text{ yield} = \frac{\text{dry weight of cellulose powder}}{\text{dry weight of sugarcane bagasse}} \times \frac{100}{1} \quad \text{---------- equation. 1}$$

2.3. CHARACTERIZATION METHOD

2.3.1. Fourier-Transform Infrared Spectroscopy (FT-IR)

FTIR analysis was carried out on SCB, extracted cellulose and NCC to detect the presence of the main organic groups that constitute the lignocellulosic cellulose structure. FT-IR analysis was carried out in the absorption band range of $4000cm^{-1} – 500cm^{-1}$ using a Bruker FT-IR Laser Class 1 spectrophotometer.

2.3.2. X – Ray Diffraction Analysis (XRD)

The x – ray diffraction analysis of the samples was evaluated using a GBC EMMA XRD Diffractometer with a monochromatic Cu Kα radiation source (λ= 1.540560Å) operating at 60 KV and 80 mA. The XRD pattern were obtained over the angular range of $2\Theta = 5^{o} –$

60° with scan step of 0.02° at a rate of 2°/min. The crystallinity index (CrI) of the samples was calculated using the peak height method by Segal *et al* (1959), as shown in equation 2 below.

$$\text{Crystallinity Index (CI)} = \frac{I_{002} - I_{am}}{I_{002}} \times \frac{100}{1} \quad \text{---------- equation 2}$$

Where I_{002} is the maximum intensity of diffraction of the (002) lattice peak at a 2Θ angle of between 21° and 23°, which represents both crystalline and amorphous materials. I_{am} is the intensity of diffraction of the amorphous material which is taken at a 2Θ angle between 18° and 20° where the intensity is at a minimum.

2.3.3. Scanning Electron Microscope (SEM) Analysis

The morphology of sugarcane bagasse, extracted cellulose and nanocrystalline cellulose produced were characterized using a Phenom proX SEM, Model number 800 – 07334. Samples were gold coated prior to recording the micrographs. The acceleration voltage was set at 15KV.

3. RESULTS AND DISCUSSIONS

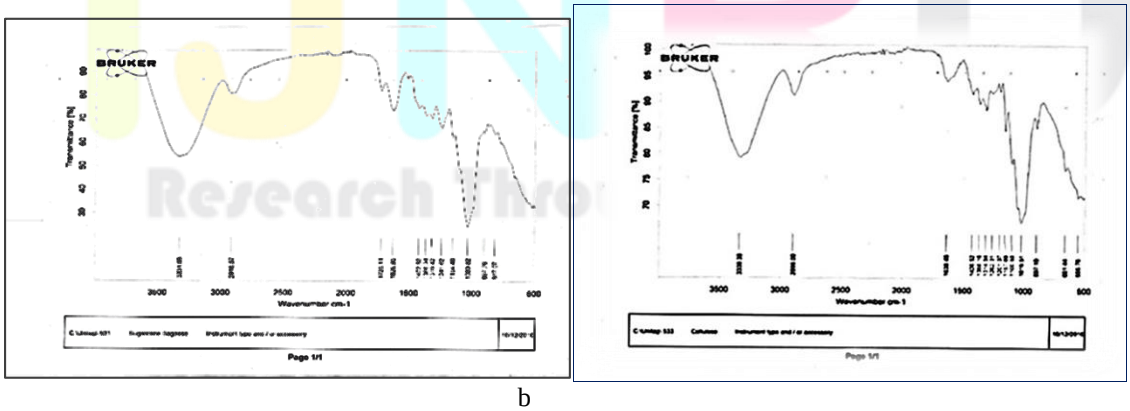
3.1 Isolation and yield of cellulose

Sugarcane bagasse which is known as lignocellulosic material contains hemicelluloses, lignin, and other components such as waxes and pectin. During the alkaline treatment, it was observed that the solution became dark and this could be as a result of dissolution of lignin, hemicelluloses and other impurities that are present in the sugarcane bagasse. Further treatment with hydrogen peroxide bleached the cellulose by removing the natural yellow colour in the bagasse until it became white. About 30g of dry sugarcane bagasse powder was initially treated, but after alkaline and peroxide treatment about 17g of cellulose was obtained. The percentage yield of cellulose isolated was about 57% as determined using the formula in equation 1 above.

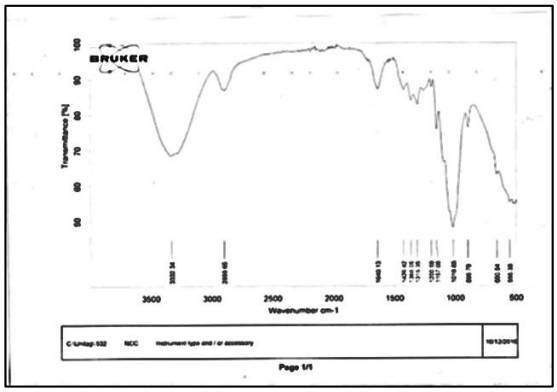
3.2 FT-IR results

The FTIR spectra of sugarcane bagasse, chemically purified cellulose and nanocrystalline cellulose are shown in figure 1 below. In all three spectra, peaks were observed around 3330cm^{-1} -3450cm^{-1}, 2850cm^{-1}-2920cm^{-1}, 1620cm^{-1}-1648cm^{-1} and 896cm^{-1}-898cm^{-1}. The broad absorption band around 3330cm^{-1} - 3450cm^{-1} corresponds to O-H stretching intramolecular and intermolecular hydrogen bond in cellulose. The peak around 2850cm^{-1} – 2920cm^{-1} is attributed to C-H stretching vibration of methylene group. The peak around 1620cm^{-1} – 1648cm^{-1} corresponds to free O-H stretching vibration of absorbed water while the peak around 896cm^{-1} – 898cm^{-1} is associated with β – glucosidic linkages of glucose ring in cellulose [31].

There are several peaks in the sugarcane bagasse spectrum which are absent from the cellulose and NCC spectra. These peaks are around 1241cm^{-1}, 1512cm^{-1} and 1725cm^{-1}. The absorption peak at 1241cm^{-1} is associated with C-O stretching vibration of the aryl group in lignin. The peak at 1512cm^{-1} is associated with C=C stretching vibration of aromatic ring in lignin while the peak at 1725cm^{-1} corresponds to the C=O stretching vibration of carboxylic groups of hemicelluloses and lignin [32]. The absence of these peaks in the extracted cellulose and NCC spectra clearly showed the removal of lignin from the sugarcane bagasse after chemical treatment. Another band of interest is the band around 1421cm^{-1}-1427cm^{-1}. This band represents CH_2 scissoring motion and it is called "the crystallinity band". Increase in intensity of this band means increase in crystallinity of the sample. In the SCB spectrum, the band appeared at 1422.83cm^{-1} while in CPC and NCC spectra it appeared at 1426.52cm^{-1} and 1426.83^{-1} respectively. It was observed that the extracted cellulose and NCC bands were a bit more intense than that of SCB which showed that there was increase in crystallinity from SCB to NCC. No difference was found between the spectra of cellulose and NCC. This suggests that no other chemical reaction resulting in changes in the functional groups occurred during the hydrolysis process.



a b



c

figure 1: FT-IR results of a (SCB), b (chemically purified cellulose), c (NCC)

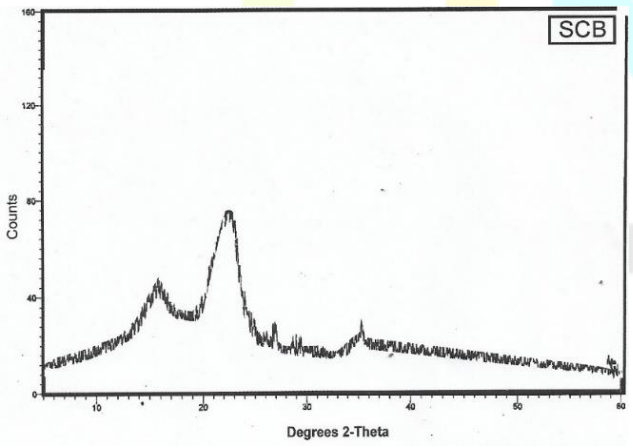
3.3. X- RAY diffraction (xrd) analysis result

Figure 2 below shows the X-ray diffraction (XRD) micrographs of sugarcane bagasse, extracted cellulose and nanocrystalline cellulose (NCC). All three diffractograms showed that the typical peaks of semicrystalline materials consist of broad amorphous region and sharp peaks of crystalline region. Each diffractogram showed three peaks around 2Θ = 16º, 22.5º, and 35º. These peaks are related to the typical type of cellulose I and correspond to the crystallographic planes that are 101, 002 and 040 respectively [33-34]. The peaks indicate the crystallinity of the material. The crystallinity index of SCB, cellulose and NCC were calculated using equation 2 above and the following results were obtained.

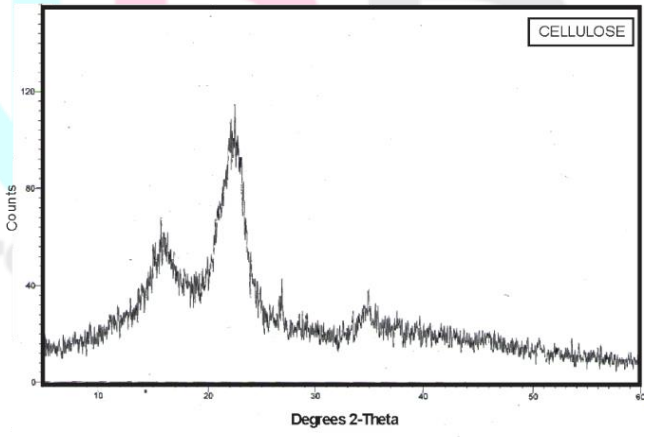
Sample	crystalinity index (CrI) %
SCB	58.9
CPC	70.4
NCC	77.1

The crystallinity index of the SCB as calculated is less than that of the NCC. The reason is because SCB contains both crystalline and amorphous regions. After hydrolysis, more amorphous regions were destroyed leaving much more crystalline region thus increased crystallinity.

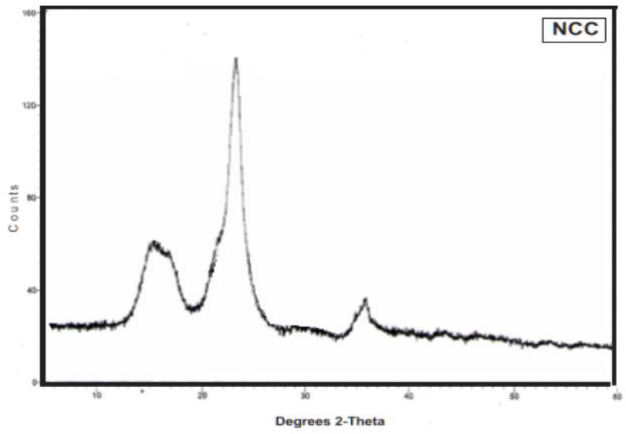
The XRD patterns shown in fig. 2 below have very clear differences. The characteristic peak at the 002 plane (2Θ = 22.5º) is associated with crysstallinity. It can be seen from the diffractograms shown that this peak is broad in SCB than in the extracted cellulose and NCC. The broadening of the peak is attributed to increased amorphousity as SCB contains all the amorphous regions predominated by lignin and hemicelluloses. After hydrolysis, the peak at the 002 plane showed increased sharpness and intensity due to the destruction of the amorphous region.



a



b

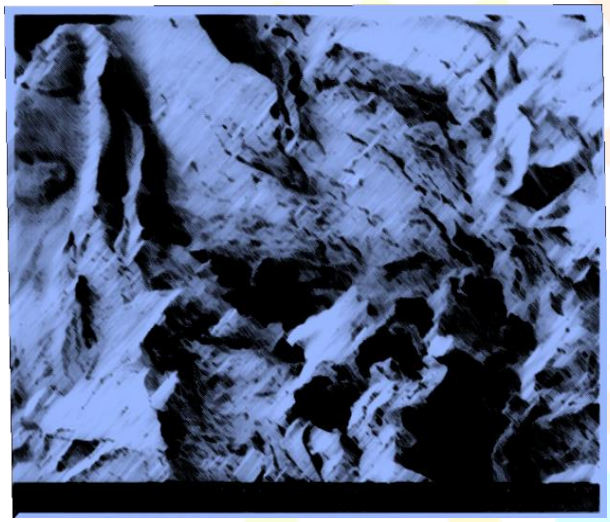


c

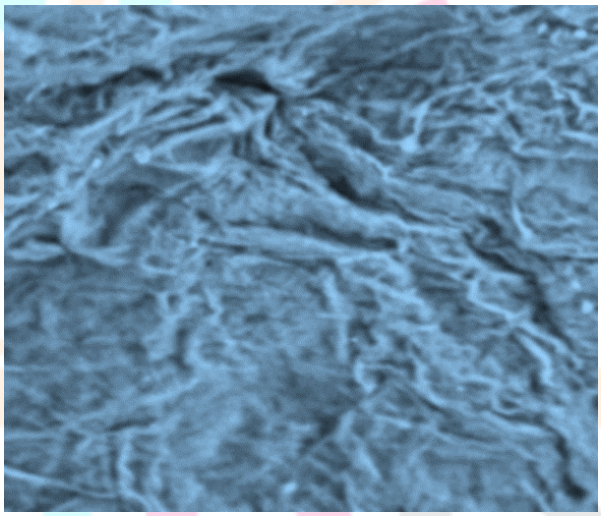
figure 2: XRD results of a (SCB), b (chemically purified cellulose), c (NCC)

3.3 SEM results

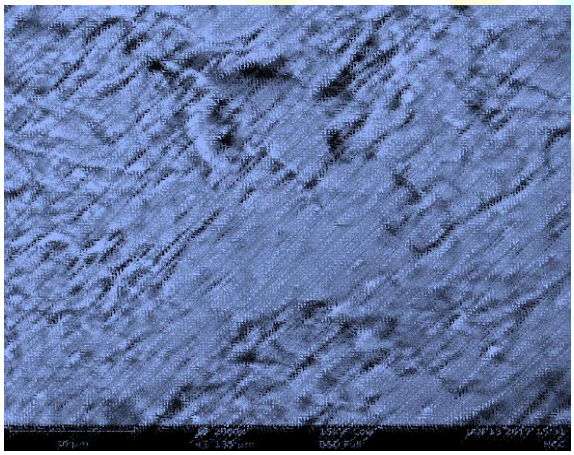
The SEM micrographs of SCB, extracted cellulose and NCC samples at a magnification of X1000 are shown in figure 3 below. The SCB micrograph in figure 3a shows a rough surface of different sizes. This can be attributed to the fact that SCB contains all the components that give plant cell its rigidity hence the rough appearance. After pre-treatment and subsequent hydrolysis there was increased homogeneity as observed in images b and c. As a result of the chemical treatment the sugarcane bagasse underwent, hemicelluloses, lignin and pectin were successfully removed. figure 3c shows agglomerated rod like nanocellulose. The agglomeration could be attributed to the method used in drying the nanocellulose.



a



b



c

figure 3: FT-IR results a (SCB), b (chemically purified cellulose), c (NCC)

4.0 CONCLUSION

This study showed that sugarcane bagasse of no economic value can be used in the synthesis of crystalline nanocellulose of high potential value. The characterization of the NCC showed agglomerated rod-like nanocellulose which could be attributed to the drying method used, and high crystallinity index.

REFERENCES

1. Trache, D. Hussin, M. H. Haafiz, M. M. and Thakur, V. K. (2017). Recent progress in cellulose nanocrystals: sources and production. *Nanoscale* 9:1763–1786.
2. Moohan, J. Stewart, S. A. Espinosa, E. Rosal, A. Rodríguez, A. Larrañeta, E. et al. (2020). Cellulose nanofibers and other biopolymers for biomedical applications. A review. *Appl. Sci.* 10:65
3. Bacakova, L. Pajorova, J. Bacakova, M. Skogberg, A. Kallio, P. Kolarova, K. and Svorcik, V. (2019). Versatile application of nanocellulose: from industry to skin tissue engineering and wound healing. *Nanomaterials* 9**(2)**:164.
4. Mohamed, M. A. Mutalib, M. A. Hir, Z. A. M. Zain, M. Mohamad, A. B. Minggu, L. J. Awang, N. A. and Salleh, W. N. W. (2017a). An overview on cellulose-based material in tailoring bio-hybrid nanostructured photocatalysts for water treatment and renewable energy applications. *Int. J. Biol. Macromol.* 103:1232–1256.
5. Lengowski, E. C. Júnior, E. A. B. Kumode, M. M. N. Carneiro, M. E.and Satyanarayana, K. G. (2019). Nanocellulose-reinforced adhesives for wood-based panels. In S*ustainable Polymer Composites and Nanocomposites*; Springer: Berlin, Germany, pp. 1001–1025.
6. Vineeth, S. Gadhave R. V. and Gadekar, P. T. (2019). Chemical modification of nanocellulose in wood adhesive. *Open J. Polym. Chem.* 9:86.
7. Mohamed, M. A. Salleh, W. Jaafar, J. Ismail, A. F. Mutalib, M. A. Mohamad, A. B. Zain, M. F. Awang, N. A. and Mohd Hir, Z. A. (2017b). Physicochemical characterization of cellulose nanocrystal and nanoporous self-assembled CNC membrane derived from *Ceiba pentandra*. *Carbohyd. Polym.* 157:1892-1902.
8. Karim, Z. Mathew, A. P. Grahn, M. Mouzon, J. and Oksman, K. (2014). Nanoporous membranes with cellulose nanocrystals as functional entity in chitosan: removal of dyes from water. *Carbohyd. Polym.* 112:668–676.
9. Fortunati, E. Puglia, D. Monti, M. Peponi, L. Santulli, C. Kenny, J.M. and Torre, L. (2013). Extraction of cellulosic nanocrystals from Phormium tenax fibres. *J. Polym. Environ*, 21:319-328.
10. Siqueira, G. Tapin–Lingua, S. Bras, J. da Silver Perez, D. and Dufresne, A. (2010). Morphological investigation of nanoparticles obtained from combined mechanical shearing, and enzymatic and acid hydrolysis of sisal fibers. *Cellulose*, 17**(6):**1147-58.
11. Ruiz, M. M. Cavaille, J.Y. Dufresne, A. Gerard, J.F. and Graillat, C. (2000). Processing and characterization of new thermoset nanocomposites based on cellulose whiskers. *Compose. Interfaces* 7**(2)**:117-131.
12. Naz, S. Ali, J. S. and Zia, M. (2019). Nanocellulose isolation, characterization and applications: a journey from non-remedial to biomedical claims. *Biodesign Manuf*. 2:187–212.
13. Eichhorn, S.J. Dufresne, A. Aranguren, M. Marcovich, N.E. Capadona, J.R. Rowan, S.J. Weder, C. Thielemans, W. Roman, M. Renneckar, S. Gindi, W. Veigel, S. Keckes, J. Yano, H. Abe, K. Nogi, M. Nakagaito, A.N. Mangalam, A. Simonsen, J. Benight, A.S. Bismarck, A. Berglund, L.A. and Peijs, T. (2010). Review: current international research into cellulose nanofibres and nanocomposites. *J. Mater. Sci.*, 45, 1 – 33.
14. Pandey, J. K. Ahn, S. H. Lee, C. S. Mohanty, A. K. and Misra, M. (2010). Recent advances in the application of Natural fiber based composites. *Macromol. Mater. Eng.* 295:975-989.
15. Beck – Candanedo, S. Roman, M. and Gray, D.G. (2005). Effect of reaction conditions on the properties and behaviour of wood cellulose nanocrystal suspensions. *Biomacromolecules*, 6, 1048 – 1054.
16. Araki, J. Wada, M. and Kuga, S. (2001). Stearic stabilization of cellulose microcrystal suspension by poly (ethylene glycol) Grafting. *Langmuir* 17:21 – 27.
17. Miller, A. F. and Donald A. M. (2003). Imaging of anisotropic cellulose suspensions using environmental scanning electron microscopy. *Biomacromolecules*, 4, 510 – 517.
18. Teixeiraa, E. M. Correaa, A. C. Manzoli, A. Liete, F. L. Oliviera, C. R. and Mattoso, L. H. C. (2010). Cellulose nanofibers from white and naturally coloured cotton fibers. *Cellulose* 17:595-606.
19. De Rodriguez, N.L.G. Thielemans, W. and A. Dufresne (2006). Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose*, 13, 261 – 270.
20. Moran, J. I. Alvarez, V. A. Cyras, V. P. and Vazquez, A. (2008). Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose* 15:149-159.
21. De Souza Lima, M. M. and Borsali, R. (2004). Rod-like cellulose microcrystals: structure, properties and applications. *Macromolecular Rapid Communications*, 25**(7):**771-781.
22. Kimura, F. Kimura, T. Tamura, M., Hirai, A. Ikuno, M. and Horri, F. (2005). Magnetic alignment of the chiral nematic phase of a cellulose microfibril suspension. *Langmuir* 21, 2034 – 2037.
23. Roman, M. and Winter, W. T. (2004). Effect of sulphonate groups from sulphuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromolecules* 5:1671-1677.
24. De Menezes, A. Jr. Siqueira, G. Ciurveto, A.A.S. and Dufresne, A. (2009). Extrusion and characterization of functionalized celluose whiskers reinforced polyethylene manocomposites. *Polymer* 50, 4552-4563.
25. Maigari, S. Y. Yakubu, M. K. Atta, A. Y. and Bukhari, M. M. (2015). Extraction and characterization of nanocrystalline cellulose from corn cob. *National Research Institute for Chemical Technology Journal.* 3-8

26. Ikhuoria, E. U. Omorogbe, S. O. Agbonlahor, O. G. and Etiuma, R. A. (2015). Preparation of nanocellulose crystals from coir fiber for template application. *American Chemical Science Journal*. **9**(1):1-11.
27. Nandi S. and Guha P. (2018). A review on preparation and properties of cellulose nanocrystal-incorporated natural biopolymer. *J. Package Technol. Res.* **2** 149–166.
28. Trache D. Tarchoun A. F. Derradji M. Hamidon, T. S. Masruchin, N. Brosse, N. Hussin, M. H. (2020). Nanocellulose from fundamentals to advanced applications. *Front. Chem.* 8:392.
29. Sun, J. X. Sun, X, F. Zhao, H. and Sun, R. C. (2004). Isolation and characterization of cellulose from sugarcane bagasse. *Polymer degradation stability*. **84**:331-339.
30. Michael Loelovich (2012). Optimal conditions for isolation of nanocrystalline cellulose particles. *Nanoscience and Nanotechnology*. **2**(2):2 – 13.
31. Wong Sak Hoi, L. and Martincigh, B. S. (2013). Sugarcane plant fibers: separation and characterization. *Industrial Crops and Products.* **47**(0):1-12.
32. Mandal, A. and Chakrabarty, D (2011). Isolation of nanocellulose from waste sugarcane bagasse and its characterization. *Carbohydr. Polymer*. 86, 1291-1299.
33. Wada, M. Heux, L. and Sugiyama, J. (2004). Polymorphism of cellulose I family: reinvestigation of cellulose IV. *Biomacromolecules.* **5**: 1385-1391.
34. Park, S. J. Baker, J. O. Himmel, M. E. Parilla, P. A. and Johnson, D. K. (2010). Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulose performance. *Biotechnol. Biofuels*. **3**:1-10.