Journal of Engineering Science and Technology
Vol. 17, No. 6 (2022) 4448 - 4458

INFLUENCE OF SODIUM HYDROXIDE CONCENTRATIONS ON REEDS (*IMPERATA CYLINDRICA*) EXTRACTION PROCESS

FATAA KUSUMATTAQIIN*, NUR WIDYA PRATIWI,
SITI NUR IZZAH, CHINDY PEBRIWIRASANTI

Department of Chemical Engineering,
Politeknik Negeri Samarinda, East-Kalimantan, Indonesia
*Corresponding Author: fataakusumattaqiin@polnes.ac.id

Abstract

Reeds (*Imperata cylindrical*) are abundant sources of cellulose which can be obtained through various processes. This study aimed to examine the effects of sodium hydroxide (NaOH) on the extraction of *Imperata cylindrical*. The extraction procedure utilized two to eight percent (w/v) sodium hydroxide concentrations. The optimization of this process was assisted by the reflux method. The FT-IR analysis revealed that the lignin peak disappeared between 1515 and 1245 cm-1. As determined by XRD, raw material and treated materials at 2 and 4 percent NaOH adopted cellulose I. In the meantime, the reeds treated with 8% NaOH transformed into cellulose II. The crystallinity index decreased dramatically after chemical treatment, from 85.93% to 43.72%. Moreover, SEM analysis revealed that treated reeds had a smoother surface than untreated reeds. In conclusion, the NaOH solutions positively affected the extraction procedure, as evidenced by a decrease in fiber size and a modification of the crystal structure.

Keywords: Cellulose I & II, Crystal transformation, *Imperata cylindrica*, Pulp, Reflux.

1. Introduction

As a non-toxic and biodegradable polymeric material, cellulose has recently gained more attention [1]. Cellulose in nature can be extracted from living creatures such as microorganisms and plants [2, 3]. Commonly, celluloses are extracted from wood or cotton. Broad applications of cellulose are applied in the paper, pharmaceutical, and textile industries. Cellulose is a polymer with each unit containing β -D-glucopyranose, connected by β-1,4-glycosidic linkage. It has a degree of polymerization (DP) ranging from 500 to 15.000 [4].

Cellulose-based crystalline allomorphs can be identified into four types, namely cellulose I, II, III, and IV. In nature, cellulose I can be found in a large number. The crystalline structure of cellulose I consist of cellulose I_α and I_β in the triclinic and monoclinic crystal structure, respectively [5]. Generally, specific chemical treatments can alter cellulose I to cellulose II by giving the treatment with aqueous NaOH (mercerization) [6]. Commonly, cellulose III and IV are derived from cellulose I and II. It is also confirmed that cellulose can be separated into cellulose I and II groups. Furthermore, cellulose I consist of I, $III_{I,}$ and IV_I, while II, $III_{II,}$ and IV_{II} are involved in cellulose II. It is also mentioned that the mechanical properties of the cellulose II group are higher than the cellulose I group [7].

The study of cellulose I to II transformation has already been reported by using cotton linter as raw material with 8-25% of aqueous NaOH. This treatment caused the degree of crystallinity to decline [8, 9]. This work investigated the effects of small concentration alkaline (2-8 % NaOH) on crystalline allomorph changes in reeds (*Imperata cylindrical*). This experiment is important because the raw material was conducted simply using the refluxing method. The polymorphic alteration of cellulose I to II has been investigated by utilizing X-ray diffraction in many cellulosic fibers [10]. Compared to cellulose I, cellulose II has a more complex structure. Paper production requires a cellulose II polymorph with a high degree of crystallinity from a production and marketing perspective [11].

2. Experimental Procedure

2.1. Material and methods

Reeds were the raw material source (*Imperata cylindrical*). The raw materials were sourced from the region. A set reflux apparatus was used for technical grade sodium hydroxide (Merck) and sodium hypochlorite (Bayclin) to maximize the extraction.

2.2. Preparation and extraction

The preparation of cellulose followed Jalaluddin et al. [12] methods. As depicted in Fig. 1, reeds were dried for a day, reduced in size to 20 mesh, and stored in an airtight container, Figs. 1(a) and (b). The delignification procedure involved a refluxing procedure. Reeds were mixed with 2% (w/v) sodium hydroxide in a refluxing flask. This procedure was carried out for one hour at 100ºC, Fig. 1(c). Reeds and sodium hydroxide solution are mixed at a ratio of 1:20 (w/v). The procedure continued by filtering the material that had been refluxed to obtain residue, Fig. 1(d).

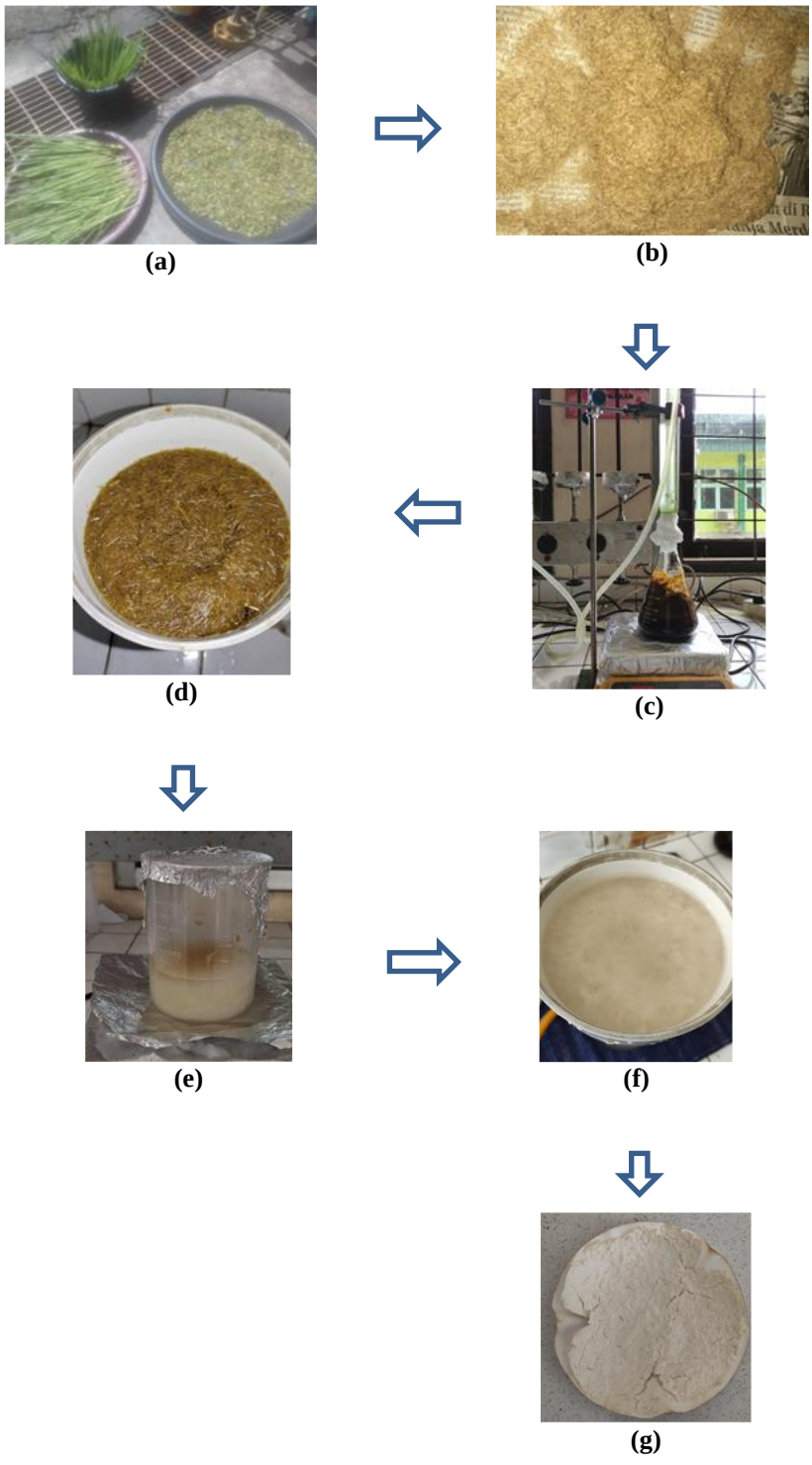


Fig. 1. Flowchart of cellulose extraction.

Filtration aims to separate liquid material from solid material (residue). Next, the residue was neutralized by washing. The washing procedure ensures that the amount of chemicals in the refluxing procedure is diminished. The remaining lignin was eliminated by adding 2.5% NaOCl to the bleaching procedure, Fig. 1(e). Residue separation and pH adjusting were done until neutral continued the procedure, Fig. 1(f). The neutrality was examined with a litmus paper. The residue was dehydrated to produce pulp cellulose, Fig. 1(g). In addition, the 4% and 8% concentrations of sodium hydroxide received the same treatment as the 2% concentration.

2.3. Crystallinity index

The crystallinity index (*CI*) of fibers was calculated by the deconvolution method from the diffraction pattern using Eq. (1):

$$CI = \frac{A_C}{A_T} \times 100 \quad (1)$$

where A_C is the area of all crystalline peaks, and A_T is the total area. The curve fitting processes were conducted using PeakFit program version 4.12. The Gaussian function was used for peak deconvolution on the XRD patterns. The r-square (r^2) larger than 0.9 was the relevant criterion.

2.4. Characterization

2.4.1. FT-IR

The functional group was observed by the FT-IR characterization Model: Thermo Scientific™ Nicolet™ iS50 FTIR. The samples were characterized using the Attenuated Total Reflection (ATR) method. The spectra were recorded from 4000 to 600 cm^{-1}.

2.4.2. XRD

The crystal structures of untreated and treated samples were characterized using X-Ray Diffraction SHIMADZU XRD-7000. The samples were beamed (2θ) from 10 to 90º. This characterization was used to ensure the changes in crystal structure between untreated reeds and treated reeds.

2.4.3. SEM

The surface morphology of samples was examined by several magnifications using SEM Model: JEOL JSM-6510LA. The fiber average size and general description before and after treatment (lignin removal) can be observed by this characterization.

3. Results and Discussion

3.1. Cellulose extraction

Table 1 displays the cellulose yield percentage at various NaOH concentrations. The bleaching (addition of NaOCl) was successfully completed. The evidence can be determined by comparing the whiteness of extracted cellulose to that of untreated reeds. This occurred due to the elimination of coloured compounds, which increases the level of whiteness [13]. The highest percentage was found when the concentration of NaOH was 4%. Furthermore, a higher percentage of

NaOH caused a decreasing trend. The plausible explanation is because of the dissolving process at lignin content [14].

Table 1. % Yield of cellulose in different concentrations of NaOH.

NaOH Concentration (%w/w)	Yield (%)
2	34.4
4	48.1
8	37.2

In the other reports, the alkaline treatment caused the liquidation process of lignin, hemicellulose, and silica liquidation. Subsequently, hydrolysing uronic and acetic acid ester occurs, and interfering with the cell wall of fibers causes cellulose inflaming. Moreover, the alpha-ether linkage between lignin and hemicellulose is demolished by alkaline solution existence [15, 16].

3.2. FT-IR characterization

The functional groups are monitored by FT-IR, as shown in Fig. 2. Bands around 3335 and 2899 cm^{-1} indicated the presence of hydroxide (OH) vibration in polyhydroxylated saccharide backbone and CH asymmetric stretching vibration in hemicellulose, lignin, and glucose monomer, respectively [17, 18]. Non-cellulosic contents before and after chemical treatments were observed in specific bands. The absorption band at 1636 cm^{-1} is related to the stretch vibration of the C=C in the aromatic ring [19], and the intensities were slightly decreased when NaOH was added. This evidence exhibited the removal of the lignin component in fiber. In addition, when higher percentages of sodium hydroxide solutions were reacted to raw material, cellulose contents increased. It can be seen at the band around 1030 $cm^{-1,}$ confirming C-O and C-H stretching vibration at cellulose structure [18, 19]. The presence of cellulose I can be detected from bands at 3335, 2899, 1429, 1316, and 896 cm^{-1} [20, 22]. The observation follows the results of Gabriel et al. [14], which were 3338 cm^{-1}, 2907 cm^{-1}, 1425 cm^{-1}, 1323 $cm^{-1,}$ and 896 cm^{-1} for bands of cellulose I. The relative increase in intensity around 895 cm^{-1} indicates cellulose II was formed [23].

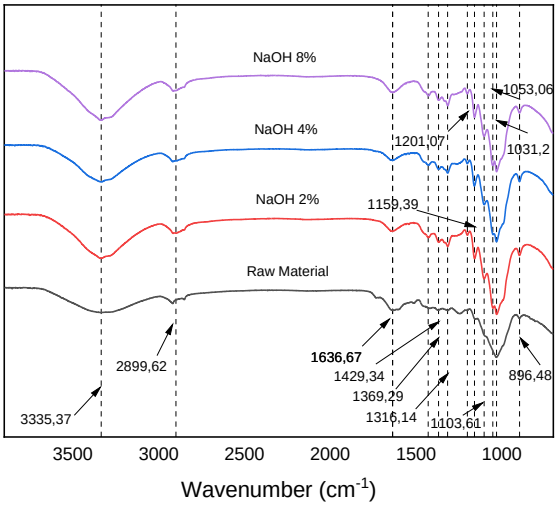


Fig. 2. FT-IR spectra of raw material and treated reeds (2, 4, and 8% NaOH).

3.3. XRD characterization

XRD examines the fiber transformation and degree of crystallinity. The diffractograms of untreated reeds and treated reeds at concentrations of 2 and 4% NaOH adopted the character of native cellulose (cellulose I), as shown in Fig. 3. Cellulose I have characteristic peaks at 2θ = 14º, 16º, 23º, and 35º [24-27]. Meanwhile, reeds at 8% concentration of NaOH transformed to cellulose II. Cellulose II has typical peaks at 2θ = 11º, 20º, and 22º, as seen in Fig. 4 [28, 29]. Similar results were obtained by El Oudiani et al. [30], showing the 2θ = 11º, 20º, and 22º for cellulose II.

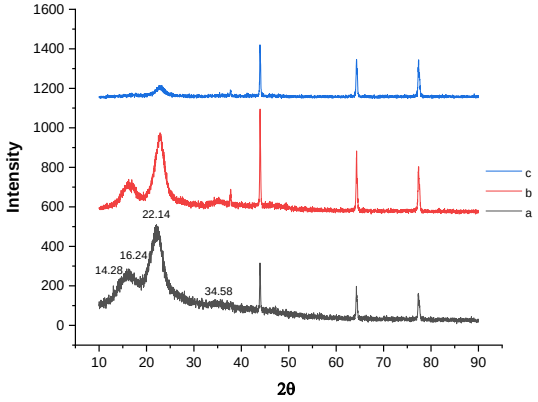


Fig. 3. XRD characterization of (a). Untreated reeds (b) treated reeds 2% of NaOH and (c) treated reeds 4% of NaOH.

In addition, the crystallinity index of untreated reeds was 85.93%. Crystallinity degrees of treated reeds 2, 4, and 8% were 82.47, 45.77, and 43.72 %, respectively. A dramatic loss of crystallinity index from untreated reeds to treated reeds was observed. It can be assumed due to the conversion of cellulose I to cellulose II [31]. The infiltration of NaOH causes this phenomenon into the cellulose fiber, which alters the crystal packing arrangement from parallel (cellulose I) to antiparallel (cellulose II). This transformation is irreversible and is accompanied by a reduction in crystallinity [14]. For commercial purposes, the treated sample with 8% NaOH is more valuable considering the high portion of cellulose II and its % crystallinity. However, low % crystallinity makes the low mechanical properties of cellulose [32].

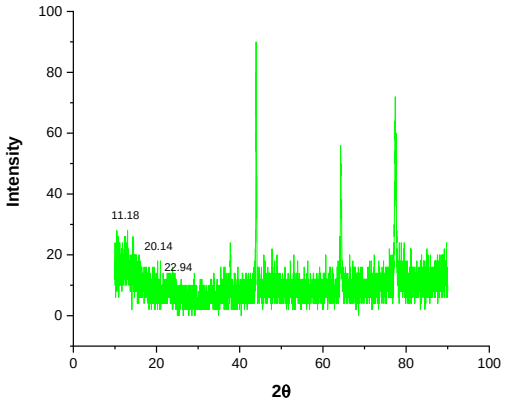
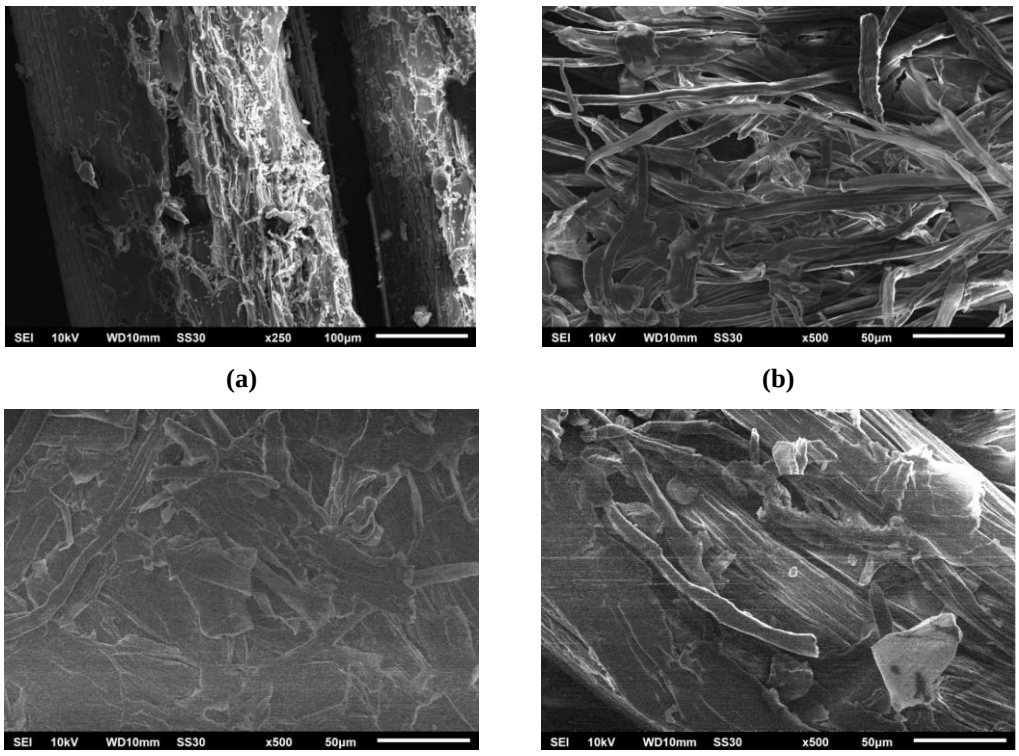


Fig. 4. Treated reeds 8% of NaOH.

3.4. Surface morphology

The morphology of untreated and treated samples was examined using SEM analysis, as depicted in Fig. 5. Images obtained using a scanning electron microscope revealed that treated reeds had fewer and smaller fibrils than untreated reeds. It was caused by eliminating non-cellulosic components and cementing substances, such as wax, hemicelluloses, and lignin, during chemical processing [33].



(a) **(b)**

(c) **(d)**

Fig. 5. SEM Analysis (a). Untreated reeds (x250 magnification) (b). Treated reeds of 2% NaOH (x500 magnification) (c). Treated reeds of 4% of NaOH (x500 magnification) and (d). Treated reeds of 8% of NaOH (x500 magnification)

The fiber diameter before and after treatment was studied. After giving the process, a decreasing trend was found from approximately 300 µm to 5 µm. The diameter of fibers, which was smaller than the raw material indicating the non-cellulosic contents in this experiment, was successfully removed [34, 35]. Moreover, Moran et al. [36] conducted cellulose extraction from sisal and reported that the diameter of untreated sisal fiber was 100-500 µm, and after chemical treatment, the diameter was reduced to 7-31 µm. In addition, Gabriel et al. [14] conducted simple, eco-friendly, and chlorine-free extraction. The results conveyed that the diameter of untreated byproduct ranged from 160 µm to 965 µm and the extracted cellulose was around 6-24 µm. This fact exhibited the removal of non-cellulosic components.

4. Conclusions

The extraction of reed cellulose was accomplished by varying the sodium hydroxide (NaOH) concentration from 2% to 8% (w/w). The bleaching agent sodium hypochlorite (NaOCl) diminished the remaining lignin. The obtained cellulose appeared whiter than the starting material. Several inferences can be drawn from the descriptions provided below.

- FT-IR spectra indicated that lignin content was diminished, confirmed by a decreasing peak around 1636 cm^{-1} corresponding to aromatic ring C=C. Furthermore, the presence of 895 cm^{-1} at 8% NaOH of extracted fiber was observed, representing cellulose II.
- At 8% NaOH, XRD analysis highlighted the crystal structure transformation from cellulose I to cellulose II. In addition, the crystallinity index decreased from 85.93% to 43.72% as more NaOH was added.
- The SEM analysis revealed that treated reeds had a smoother appearance and were smaller than untreated reeds. It is caused by the loss of non-cellulosic material.
- Further investigation is needed to compose a composite to enlarge physical properties.

Nomenclatures

cm^{-1}	Wavenumber
D	Dextro
w/v	Weight to volume
w/w	Weight to weight

Greek Symbols

β	Beta glycosidic bond
θ	Angel beam

Abbreviations

FT-IR	Fourier Transform Infra-Red
NaOCl	Sodium Hypochlorite
NaOH	Sodium Hydroxide
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction

References

1. Trache, D.; Hussin, M.H.; Chuin, C.T.H.; Sabar, S.; Fazita, M.R.N.; F.A.Taiwo, O.; Hassan, T.M.; and Haafiz, M.K.M. (2016). Microcrystalline cellulose: Isolation, characterization and bio-composites application - A review. *International Journal of Biological Macromolecules*, 93(A), 789-804.
2. Mischnick, P.; and Momcilovic, D. (2010). Chemical structure analysis of starch and cellulose derivatives. *Advances in Carbohydrate Chemistry and Biochemistry*, 64, 117-210.
3. Khan, M.Z.K.; Hasan, A.K.; Anwar, M.P.; and Islam, M.S. (2017). Weeding regime and plant spacing influence on weed growth and performance of

transplant aman rice variety Binadhan- 7. *Fundamental and Applied Agriculture*, 2(3), 331-339.

4. Mittal, A.; Katahira, R.; Himmel, M.E.; and Johnson, D.K. (2011). Effects of alkaline or liquid-ammonia treatment on crystalline cellulose: changes in crystalline structure and effects on enzymatic digestibility. *Biotechnology for Biofuels*, 4:41, 1-16.
5. Atalla, R.H.; and Vanderhart, D.L. (1984). Native cellulose: a composite of two distinct crystalline forms. *Science*, 223(4633), 283-285.
6. Dinand, E.; Vignon, M.; Chanzy, H.; and Heux, L. (2002). Mercerization of primary wall cellulose and its implication for the conversion of cellulose I→cellulose II. *Cellulose*, 9(1), 7-18.
7. Ishikawa, A.; and Okano, T. (1997). Fine structure and tensile properties of ramie fibres in the crystalline form of cellulose I, II, Illl and IV_I *Polymer*, 38(2), 463-468.
8. Fengel, D.; Jakob, H.; and Strobel, C. (1995). Influence of the alkali concentration on the formation of cellulose II. Study by x-ray diffraction and FTIR spectroscopy. *Holzforschung*, 49, 505-511.
9. Fink, H.-P.; Hofmann, D.; and Philipp, B. (1995). Some aspects of lateral chain order in cellulosics from X-ray scattering. *Cellulose*, 2(1), 51-70.
10. Zhou, L.M.; Yeung, K.W.; Yuen, C.W.M.; and Zhou, X. (2004). Characterization of ramie yarn treated with sodium hydroxide and crosslinked by 1. 2,3,4-butanetetracarboxylic acid. *Journal of Applied Polymer Science*, 91(3), 1857-1864.
11. Guptaa, P.K.; Uniyal, V.; and Naithani, S. (2013). Polymorphic transformation of cellulose I to cellulose II by alkali pretreatment and urea as an additive. *Carbohydrate Polymers*, 94(2), 843-849.
12. Jalaluddin; Dewi, R.; and Irda, F. (2014). Pengaruh waktu perebusan dan konsentrasi pelarut terhadap produksi pulp dari ilalang. *Teknologi Kimia Unimal*, 3(2), 23-32.
13. Watkins, D.; Nuruddin, M.; Hosur, M.; Tcherbi-Narteh, A.; and Jeelani, S. (2015). Extraction and characterization of lignin from different biomass resources. *Journal of Materials Research and Technology*, 4(1), 26-32.
14. Gabriel, T.; Belete, A.; Syrowatka, F.; Neubert, R.H.H.; and Gebre-Mariam, T. (2020). Extraction and characterization of celluloses from various plant byproducts. *International Journal of Biological Macromolecules*, 158, 1248-1258.
15. Abdel-Halim, E.S. (2014). Chemical modification of cellulose extracted from sugarcane bagasse: Preparation of hydroxyethyl cellulose. *Arabian Journal of Chemistry*, 7(3), 362-371.
16. Vu, N.D.; Tran, H.T.; Bui, N.D.; Vu, C.D.; and Nguyen, H.V. (2017). Lignin and cellulose extraction from Vietnam's rice straw using ultrasound-assisted alkaline treatment method. *International Journal of Polymer Science*, Volume 2017, Article ID 1063695, 1-8.
17. Tarchoun, A.F.; Trache, D.; and Klapötke, T.M. (2019). Microcrystalline cellulose from Posidonia oceanica brown algae: Extraction and characterization. *International Journal of Biological Macromolecules*, 138, 837-845.

18. Gabriel, T.; Belete, A.; Syrowatka, F.; Neubert, R.H.H.; and Gebre-Mariam, T. (2020). Extraction and characterization of celluloses from various plant byproducts. *International Journal of Biological Macromolecules*, 158, 1248-1258.
19. Zain, N.F.M.; Yusop, S.M.; and Ahmad, I. (2014). Preparation and characterization of cellulose and nanocellulose from pomelo (*Citrus grandis*) albedo. *Journal of Nutrition & Food Sciences*, 5(1), 1-4.
20. Veeramachineni, A.K.; Sathasivam, T.; Muniyandy, S.; Janarthanan, P.; Langford, S.J.; and Yan, L.Y.(2016). Optimizing extraction of cellulose and synthesizing pharmaceutical grade carboxymethyl sago cellulose from malaysian sago pulp. *Applied Sciences*, 6(6), 170, 1-18.
21. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; and Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*, 86(12-13), 1781-1788.
22. Haafiz, M.K.M.; Eichhorn, S.J.; Hassan, A.; and Jawaid, M.. (2013). Isolation and characterization of microcrystalline cellulose from oil palm biomass residue. *Carbohydrate Polymers*, 93(2), 628-634.
23. Hurtubise, F.G.; and Krassig, H. (1960). Classification of fine structural characteristics in cellulose by infared spectroscopy. use of potassium bromide pellet technique. *Analytical Chemistry*, 32(2), 177-181.
24. Khalifa, B.A.; Abdel-Zaher, N.; and Shoukr, F.S. (1991). Crystalline character of native and chemically treated Saudi Arabian cotton fibers. *Textile Research Journal*, 61(10), 602-608.
25. Davidson, T.C.; Newman, R.H.; and Ryan, M.J. (2004). Variations in the fibre repeat between samples of cellulose I from different sources. *Carbohydrate Research*, 339(18), 2889-2893.
26. Ouajai, S.; and Shanks, R.A. (2005). Composition, structure and thermal degradation of hemp cellulose after chemical treatments. *Polymer Degradation and Stability*, 89(2), 327-335.
27. El Oudiani, A.; Sghaier, R.B.; Chaabouni, Y.; Msahli, S.; and Sakli, F. (2012). Physico-chemical and mechanical characterization of alkali-treated A*gave americana L*. fiber. *The Journal of The Textile Institute*, 103(4), 349-355.
28. Ass, B.A.P.; Belgacem, M.N.; and Frollini, E. (2006). Mercerized linters cellulose: Characterization and acetylation in N,N-dimethylacetamide/lithium chloride. *Carbohydrate Polymers*, 63(1), 19-29.
29. Qin, C.; Soykeabkaew, N., Xiuyuan, N.; and Peijs, T. (2008). The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites. *Carbohydrate Polymers*, 71(3), 458-467.
30. El Oudiani, A.; Chaabouni, Y.; Msahli, S.; and Sakli, F. (2011). Crystal transition from cellulose I to cellulose II in NaOH treated Agave americana L. fibre. *Carbohydrate Polymers*, 86(3), 1221-2129.
31. Revol, J.F.; Dietrich, A.; and Goring, D.A.I. (1987). Effect of mercerization on the crystallite size and crystallinity index in cellulose from different sources. *Canadian Journal of Chemistry*, 65(8), 1724-1725
32. Az-Zahra, N.; Rahmi, R.; and Lubis, S. (2019). Reinforcement of chitosan film using cellulose isolated from grass (imperata cylindrica). *Journal of Physics: Conference Series*, 1402(5), 055039, 1-5.

33. Deepa, B.; Abraham, E.; Cherian, B.M.; Bismarck, A.; J.Blaker, J.; Pothan, L.A.; Leao, A.L.; de Souza, S.F.; and Kottaisamyd, S.M. (2011). Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion. *Bioresource Technology*, 102(2), 1988-1997.
34. Nazir, M.S.; Wahjoedi, B.A.; Yussof, A.W.; and Abdullah, M.A. (2013). Eco-friendly extraction and characterization of cellulose from oil palm empty fruit bunches. *BioResource*, 8(2), 2161-2172.
35. Deep, B.; Abraham, E.; Cherian, B.M.; Bismarck, A.; Blaker, J.J.; Pothan, L.A.; A.L. Leao, S.F.; de Souza, S.F.; and Kottaisamy, M. (2011). Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion. *Bioresorces Technology*, 102(2), 1988-1997.
36. Morán, J.I.; Alvarez, V.A.; Cyras, V.P.; And Vázquez, A. (2007). extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose*, 15(1), 149-159