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Preparation and Characterization of Cellulose and Nanocellulose from Agro-industrial Waste - Cassava Peel

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Abstract. Cassava peel is an agro-industrial waste which is available in huge quantities in Lampung Province of Indonesia. This work was conducted to evaluate the potential of cassava peel as a source of cellulose and nanocellulose. Cellulose was extracted from cassava peel by using different chemical treatment, and the nanocellulose was prepared by hydrolysis with the use of sulfuric acid. The best methods of cellulose extraction from cassava peels are using alkali treatment followed by a bleaching process. The cellulose yield from this methods was 17.8% of dry base cassava peel, while the yield from nitric and sulfuric methods were about 10.78% and 10.32% of dry base cassava peel respectively. The hydrolysis was performed at the temperature of 50 °C for 2 hours. The intermediate reaction product obtained after each stage of the treatments was characterized. Fourier transform infrared spectroscopy showed the removal of non-cellulosic constituent. X-ray Diffraction (XRD) analysis revealed that the crystallinity of cellulose increased after hydrolysis. Morphological investigation was performed using Scanning Electron Microscopy (SEM). The size of particle was confirmed by Particle Size Analyzer (PSA) and Transmission Electron Microscopy (TEM).

1. Introduction

Recently, there is an increasing tendency towards more useful utilization of agro-industrial waste, such as sugarcane bagasse, cassava bagasse, and cassava peel, as raw materials for industrial use [1.2]. Cassava (Manihot esculenta Cranz) is the fifth most abundant starch crop produced in the world, the third most important food source for inhabitants in the tropical areas [3] and Indonesia is the third most cassava producing country in the world with around 24.5 million tonnes production in 2015 [4]. Cassava bagasse and cassava peel produced in large quantities by industrial tapioca starch. The bagasse is usually used as animal feed whereas cassava peel is very rarely used and wasted. The peels of cassava contribute to 15% of the tubular cassava root weight and the abundant production of this crop has resulted in the yield of a huge amount of peels. Cellulose content in cassava peel is quite promising at around 40-55% of dry base peel [5,6]. Therefore, the cassava peel has a potential as a source of cellulose.

Cellulose is one of the most abundant, renewable and biodegradable polymers [3]. Cellulose is a natural polymer which insoluble in water because of its long chain and high molecular weight (more than 500.000 Da). Cellulose in nanometers dimension has a range size of 10 nm to 350 nm. Nanocellulose are nanoparticles having outstanding mechanical properties can be used to enhance the mechanical properties of polymer nanocomposites [7].

Among the various methods for preparing nanocellulose, the acid hydrolysis is the most distinguished and broadly used [8]. This method is convenient and fast to generate nanocellulose with a preferable property. This process breaks the irregular and amorphous parts of cellulose, removing single and well-defined crystal. The important parameters that affect the properties of nanocellulose are the temperature, time of reaction, acid nature and ratio of the acid to cellulose. There are several stages in acid hydrolysis procedure i.e. strong acid hydrolysis of cellulose under controlled conditions; addition of water to stop hydrolysis process; centrifugation; dialysis with cellulosic membrane; ultrasonication and drying of the suspension [9,10].

The performance of nanocellulose as a reinforcing agent is dependent on the properties of cellulose and the properties of cellulose is depend mainly on source of original cellulose. Therefore, the development of nanocellulose from various source of cellulose is relevant. Thus, the purpose of this study was conducted to examine the potential of an agro-industrial waste i.e. cassava by isolating cellulose from its peel and preparing nanocellulose and then followed by determining its physicochemical and structural properties.

2. Experimental

2.1. Material

Cassava peel (CP) was collected from cassava crisp home industry located in Bandar Lampung, Lampung Province, Indonesia. The chemical used for cellulose isolation and nanocellulose preparation were: sodium hypochlorite, sodium hydroxide, sulfuric acid, nitric acid, sodium chlorite, sodium nitric, sodium sulfite, pure microcrystalline cellulose. All chemicals were pro analysis grade.

2.2. Methods

2.2.1. Isolation of cellulose. The isolation of cellulose from cassava peel was obtained by three different methods. Prior to cellulose isolation, cassava peel was separated from its outer skin, washed and milled into pulp. This pulp was then dried in sunlight for 2 days until reach a constant weight. (*Nitric methods)* 10 g dried pulp was dissolved in 200 mL of 3.5% HNO_3 and added 1.5 mg $NaNO_2$. Sample mixture is heated at 90 °C for 2 h with stirring. Then the mixture was filtered and the obtained residue was washed until neutral. The residue was refluxed with a mixture of 150 mL 2% NaOH and 2% $NaSO_3$ (1:1) solution for 2 hours. And then, the mixture was filtered and washed until the filtrate of obtained residue become neutral. The residue was refluxed use 2% $NaClO_2$ solution with a few drops of glacial acetic acid for 30 minutes. *(Sulphuric methods)* 10 g of dried pulp was dissolved in 200 mL of 0.5M H_2SO_4 by heating at 90 °C for 2 h with stirring. Subsequently the mixture is filtered and the obtained residue is washed until neutral. The next step is a bleaching process wherein the residue refluxed use 2% $NaClO_2$ solution plus a few drops of glacial acetic acid for 30 minutes. *(Alkali methods)* 10 g of dried pulp was refluxed with 200 mL of 4% sodium hydroxide for 2 hours with constant stirring at 90 °C. The mixture was bleached with 100 mL of 4% (w/v) sodium hypochlorite for 1 hour with constant stirring at 80 °C. The residue was washed with distilled water until a neutral pH, and it was dried at room temperature for 2-3 days.

2.2.2. Preparation of nanocellulose. Isolated cellulose from cassava peel was hydrolyzed with sulfuric acid with a ratio of cellulose to sulfuric acid 1:25. The hydrolysis of cellulose was carried out in 45% (w/w) sulfuric acid solution at 50 ^{o}C for 2 hours. The hydrolysis process was quenched by adding excess distilled water (250 mL) to the reaction mixture. The produced colloidal suspension was centrifuged at 14,000 rpm for 10 minutes at -4 ^{o}C. Then, it was dialyzed for 5 days to neutralize and eliminate the sulfate ions. The neutral colloidal suspension was sonicated for 30 minutes to homogenize the generated nanocellulose.

2.2.3. Cellulose and nanocellulose characterization. The purity of cellulose in isolated cellulose was determined by TAPPI 203 cm-99 methods. The morphology of untreated cassava peel, CP cellulose, and CP nanocellulose were characterized by SEM Zeiss MA 10. All samples were coated with gold prior to examination. The FTIR spectra of cellulose and nanocellulose were recorded on Fourier Transform Infrared Spectrometer Shimadzu Prestige 21. The samples were blended with KBr powder and then pressed to become thin pellets. The sample was measured in the wavelength range from 4000 cm^{-1} to 500 cm^{-1}. The particle size of nanocellulose was determined by Particle Size Analyzer (PSA) with a Beckman Coulter Delsa^{TM} Nano. The nanocellulose was diluted with distilled water and inserted into the cuvette. The measurements were done at room temperature with the measurement range from 10 nm until 4000 nm. The morphology measurements of the nanocellulose colloids were carried out on a Transmission Electron Micrograph (TEM), JEOL JEM 1400. The X-ray diffraction data were collected using Bruker D8 Advance. The X-ray source is a 2.2 kW Cu anode long fine focus ceramic X-ray tube. The running conditions for the X-Ray tube are 40 kV and 40 mA.

3. Result and Discussion

3.1. Cellulose isolation

Three methods to isolate the cellulose from cassava peel have been tested where the result can be seen in Table 1. It is shown clearly that the alkali method is the best among the three methods tested.

Table 1. Yield percentage and cellulose purity from different methods

Methods	Yield, %	Cellulose, %
Nitric	10.78	92.83
sulphuric	10.32	90.87
Alkali	17.80	93.24

Fig. 1a shows the physical appearance of the CP raw material before any processing. After isolation of cellulose from the raw material, the result was a yellowish white cotton-like material (Fig. 1b). The purity of cellulose obtained by isolation of the cassava peel was fairly high with 90-94% of cellulose. The alkali method to produce cellulose is far more efficient than the two other methods. This is due to the minimum using of chemical in this method and at the other side; many small particles were discarded during washing step after strong acid hydrolysis at nitric and sulphuric methods.

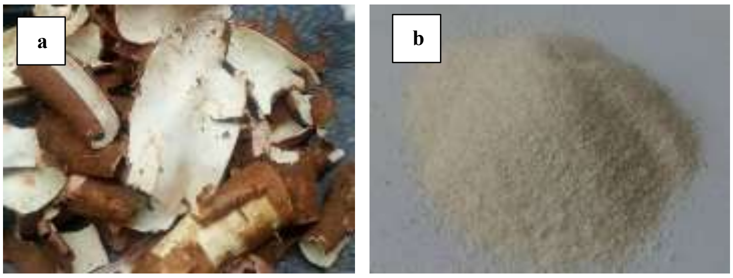

Figure 1. The image of (a) Cassava peel, and (b) CP cellulose,

3.2. FTIR Analysis

FTIR spectroscopy was used to confirm that the lignin and hemicellulose have been removed during cellulose isolation step through analysis of its functional groups. The FTIR spectra of untreated cassava peel and cassava peel cellulose are displayed in Fig. 2.

Based on FTIR spectrum, there are two peaks in untreated cassava peel which is not found in the spectrum of its cellulose. The peaks are 1502 cm^{-1}, and 1738 cm^{-1}. The peak at 1502 cm^{-1} is attributed to the C=C stretching vibration from the aromatic ring of lignin and the peak at around 1738 cm^{-1} is the C=O stretching vibration of carboxylic groups of hemicellulose and lignin [3,11,12].

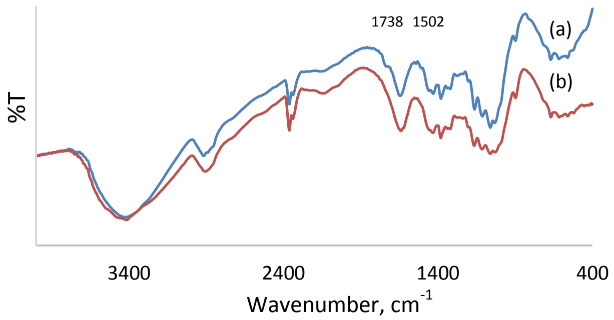

Figure 2. FTIR spectra untreated (a) cassava peel and (b) CP cellulose

3.3. *Preparation of nanocellulose*

Fig. 3 displays images of nanocellulose produced from CP isolated cellulose in the form of suspension colloid, gel and powder. The transparent gel was obtained after cold centrifugation at 14,000 rpm. The gel was freeze-dried for 24 hours to produce a white nanocellulose powder.

Figure 3. The image of nanocellulose in a form of (a) colloid, (b) gel and (c) powder

3.4. *Morphology study*

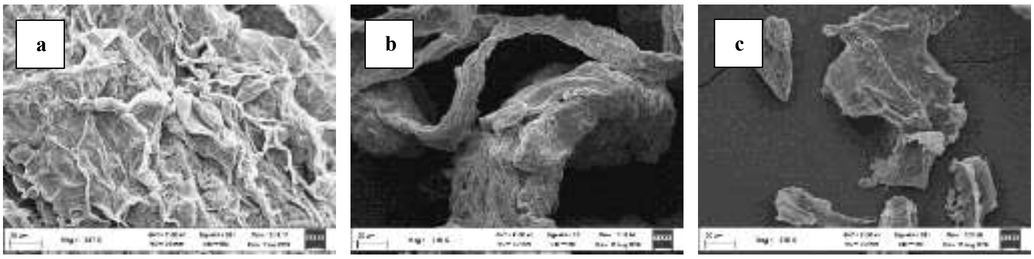

Figure 4. SEM micrograph of (a) untreated CP, (b) CP isolated cellulose and (c) CP nanocellulose

Scanning electron microscopy (SEM) was used to investigate the morphology of cassava peel, CP cellulose, and CP nanocellulose. The change of fiber surface after the isolation of cellulose was shown in Fig. 4 (a-b). It is shown that the granules of starch in untreated cassava peel (Fig. 4a) were disappeared after chemical treatment. Dried untreated cassava peel contain around 60-70% starch and 20-30% others impurities which were eliminated during cellulose isolation processes.

3.5. *Particle size distribution*

The size of nanoparticle was measured by Particle Size Analyzer with the mostly particle size around 150 nm (Fig. 5). However, the TEM images of nanocellulose confirm the size of particle was below 150 nm. The size varies from 100-300 nm in length and 3-8 nm in width (Fig. 6).

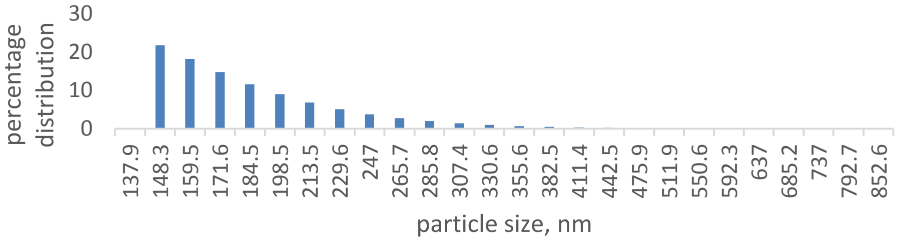

Figure 5. Particle size distribution of CP nanocellulose

3.6. *Transmission Electron Microscopy (TEM)*

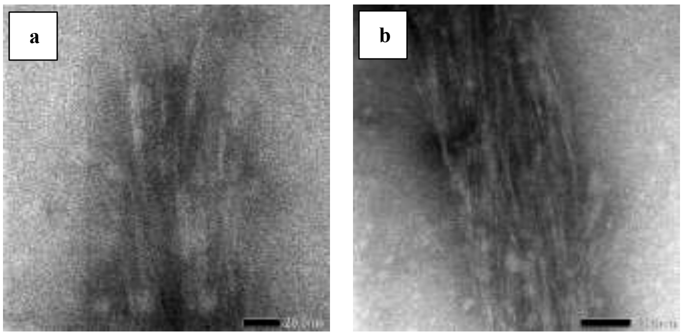

Figure 6. TEM images of CP nanocellulose in (a) 150,000 and (b) 80,000 times magnification

Preparation of nanocelulose from cassava peel was succesful as confirmed by obviously a needle-like (whiskers) nanoparticles [13,14]. Fig. 6a and 6b report TEM micrographs of the nanocellulose in 150,000 and 80,000 times magnification, respectively. The images show individual and aggregate nanocrystals. The appearance of aggregate nanoparticles is due to strong hydrogen bonding established between the whiskers [13]. It is also confirmed by the SEM image of the agglomerate particles (Fig. 4c).

3.7. *Crystallinity*

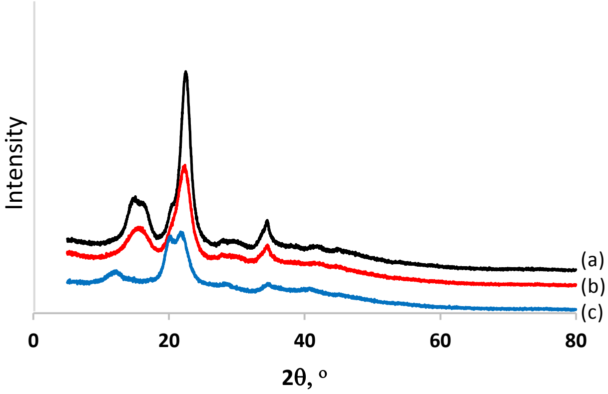

Figure 7. XRD of (a) pure MMC, (b) CP nanocellulose and (c) CP isolated cellulose

The crystallinity of isolated cellulose, nanocellulose and pure microcrystalline cellulose (MCC) were analyzed by X-ray diffraction (XRD). The XRD patterns show that there was a change in crystallinity type of cellulose before and after acid hydrolysis. Two major 2θ value of around 20^{o} and 22^{o} of CP isolated cellulose (Fig. 7c) are characteristic of cellulose II type crystalline weather the major intensity peak at around 22.6^o of CP nanocellulose (Fig. 7b) is related to cellulose I crystalline structure [15]. However, the XRD diffractogram of CP nanocellulose is very similar with pure MCC (Fig. 7a) and this is as evidence of the purity of the obtained nanocellulose.

Table 2 shows the crystallinity index and major XRD diffractogram peak of the samples. There was an increase of crystallinity index of CP isolated cellulose after acid hydrolysis due to the removal of remaining amorphous hemicellulose and lignin.

Table 2. Major peak and crystallinity index of CP isolated cellulose and nanocelulose

Samples	Major intensity (2θ), °	Cellulose type	Crystallinity index, %
CP isolated cellulose	20.2; 21.9; 34.7	II	50.5
CP nanocellulose	15.4; 22.3; 27.8; 34.4	I	51.2
Pure Microcrystalline cellulose	14.9; 16.0; 22.5; 28.0; 34.5	I	61.9

4. Conclusion

Cellulose can be isolated from the cassava peel excellently via alkali treatment followed by bleaching process. Nanocellulose was successfully obtained by sulfuric acid hydrolysis of the cassava peel isolated cellulose. According to TEM images, it was possible to produce a needle-like nanoparticle with sizes varying from 100-300 nm in length and 3-8 nm in width. Such a value is adequate for application CP nanocellulose as nanofillers in polymer matrices.

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References

[1] Wulandari W T, Rochliadi A and Arcana I M 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* **107** *012045*
[2] Teixeira E M, Curvelo A A S, Correa A C, Marconcini J M, Glenn G M and Mattoso L H C 2012 *Ind. Crops Prod.* **37** 1 61-68
[3] Mandal A and Chakrabarty D 2011 *Carbohydr. Polym.* **86** 1291-1299
[4] FAO 2015 *Food Outlook Biannual Report on Global Food Market November 2015*
[5] Daud Z, Awang H, Kassim A S M, Hatta M Z M, and Aripin A M 2014 *Adv. Mat. Res.* **974** 384-388
[6] Versino F, Lopez O V and Garcia M A 2015 *Ind. Crops Prod.* **65** 79–89
[7] Martoïa F, Dumont P J, Orgéas L, Belgacem M N, and Putaux J L 2016 *RSC Adv.* **6** 47258
[8] Sheltami R M, Abdullah I, Ahmad I, Dufresne A and Kargarzadeh H 2012 *Carbohydr. Polym.* **88** 772-779
[9] Brinchi L, Cotana F, Fortunati E and Kenny J M 2013 *Carbohydr. Polym.* **94** 154-169
[10] Dong X M, Revol J F, and Gray D G 1998 *Cellulose* **5** 19-32
[11] Sain M and Panthapulakkal S 2006 *Ind. Crops Prod.* **23** 1-8
[12] Garside P and Wyeth P *Studies in Conservation* **48** 269-275
[13] Neto W P F, Silvérioa H A, Dantas N O, and Pasquini D 2013 *Ind. Crops Prod.* **42** 480–488
[14] Johar N, Ahmad I, and Dufresne A 2012 *Ind. Crops Prod.* **37** 93-99
[15] Zain N F M, Yusop S M, Ahmad I 2012 *J. Nutr. Food Sci.* **5** 334