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Production of Nanocellulose from Kepok Banana Peel Waste Using Acid Hydrolysis Method

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Abstract

Research on the production of nanocellulose from kepok banana peel waste has been carried out using the Acid Hydrolysis method with H_2SO_4 Sulfuric Acid. This study aims to determine the effect of giving H_2SO_4 on kepok banana peels and the crystal structure and surface morphology of nanocellulose on kepok banana peels. The production of nanocellulose was carried out in three stages: delignification using 10% NaOH, bleaching using 10% H_2O_2, and isolation of nanocellulose using H_2SO_4 with various concentrations of 5, 10, 15, and 20%. This research uses X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) as its characterization. The resulting crystallite size ranges from 3.58 to 4.15 nm, producing a lump-like morphological structure.

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Abstrak

Penelitian pembuatan nanoselulosa dari limbah kulit pisang kepok telah dilakukan dengan metode Hidrolisis Asam dengan Asam Sulfat H_2SO_4. Penelitian ini bertujuan untuk mengetahui pengaruh pemberian H_2SO_4 pada kulit pisang kepok serta terhadap struktur kristal dan morfologi permukaan nanoselulosa pada kulit pisang kepok. Pembuatan nanoselulosa dilakukan dalam tiga tahap yaitu delignifikasi menggunakan NaOH 10%, bleaching menggunakan H_2O_2 10% dan isolasi nanoselulosa menggunakan H_2SO_4 dengan variasi konsentrasi 5, 10, 15, dan 20%. Penelitian ini menggunakan *X-Ray Diffraction* (XRD) dan *Scanning Electron Microscopy* (SEM) sebagai karakterisasinya. Ukuran kristalit yang dihasilkan berkisar antara 3,58 hingga 4,15 nm dan menghasilkan struktur morfologi seperti gumpalan.

1. Introduction

Cellulose is an organic compound that is the main constituent of plant cell walls. Approximately 33% of all plant matter is cellulose (Singh et al., 1993). Cellulose-based materials are often used because they have good mechanical properties such as high strength and tensile modulus, high purity, high water binding capacity, and good tissue structure (Kennedy, 1993). Cellulose production is an almost inexhaustible raw material for the demand for environmentally friendly and biocompatible products (Kim et al., 2015). Most cellulose combines with lignin and other polysaccharides, such as hemicellulose, in plant cell walls (Klemm, 1998).

Nanocellulose is one of the cellulose materials that has been developed and has the potential to be developed because of its good mechanical properties. Its raw material comes from abundant and renewable natural resources. Nanocellulose has a diameter of 1-100 nm and a length of 500-2000 nm. Nanocellulose can be used for various end products such as paper, cardboard, cosmetics, health, optical equipment, and pharmaceuticals. Several techniques to develop cellulose into nanocellulose include acid hydrolysis, enzymatic hydrolysis, and mechanical processes (Cherian et al., 2010). Generally, Nanocellulose s divided into three types, namely Cellulose Nanocrystals (CNC), Cellulose Nanofibrils (CNF), and Cellulose Microfibrils (MFC) (Lin and Dufresne., 2014). CNC particles generally have a width of 5-70 nm and a length of 100-250 nm and are highly crystalline, with 54-88% (Moon et al., 2011). Meanwhile, CNF generally has a diameter of 5-60 nm (Janoobi et al., 2015). The most common method for obtaining CNC is chemical hydrolysis using acids such as HCl and H_2SO_4 (Zain et al., 2015). While the method to obtain CNF is to use enzymatic hydrolysis (Fritz et al., 2015). In its application in the medical field, nanocellulose is often used

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in drug delivery (Trache et al., 2015). Meanwhile, the application of nanocellulose in agriculture is to protect seeds and plants. Nanocellulose composite coatings are valuable because of their mechanical properties and biodegradability (Lavicola et al., 2017).

A Banana is a relatively large plant with large leaves with the Musaceae tribe. Indonesia has the seventh-largest banana production globally, and the kepok banana is one of Indonesia's most famous banana types. Bananas are often processed into chips, sponge cake, molen, etc. The processing, of course, produces waste such as banana peels. In general, banana peel waste contains cellulose, so that banana peel waste can be used as a primary material for manufacturing nanocellulose (Sylvia, 2015).

2. Research methods

Tools and materials used in this research are analytical balance, beaker, spatula, plastic wrap, measuring cup, Erlenmeyer flask, magnetic stirrer, hotplate, centrifuge, litmus paper, water bath, ultrasonic cleaner, stative, petri dish, aluminum foil, oven, mortar, tissue, and filter. At the same time, the materials used in this study were banana peel waste, NaOH, Aquades, H_2O_2, and H_2SO_4 with various concentrations of 5,10,15, and 20%. Meanwhile, the characterizations used in this study were XRD and SEM.

2.1 Sample Preparation

Kepok banana peels are dried at 80-90°C until the banana peels dry, and then the banana peels are cut into several pieces. Then the banana peel waste is blended until it becomes a powder and is ready to be used as the primary material for manufacturing nanocellulose.

2.2 Delignification

Delignification aims to separate lignin and hemicellulose from cellulose using 5 grams given a solution of 10% NaOH (5 ml), then left for 24 hours. After that, the NaOH is removed, and the banana peel powder is filtered using a filter so that it is ready to be used for the next stage.

2.3 Bleaching

In this process, 5 grams of kepok banana peel waste is soaked in a 10% H_2O_2 solution for 24 hours. After that, the H_2O_2 solution was removed and separated from the banana peel powder. Then, the banana peel powder was washed with distilled water until the color turned white and the pH was neutral.

2.4 Nanocellulose insulation

The acid hydrolysis method is carried out by drying the banana peel powder first in the oven at room temperature. After drying, the banana peel powder was weighed with an analytical balance to determine the weight of the sample after being treated in the previous stages. Then, the banana peel powder was given a solution of H_2SO_4 With various concentrations of 5,10,15, and 20% and then cooked in a water bath for 3.5 hours at 50°. The precipitate was neutralized with a centrifuge until the pH became neutral, after which the sample was put in an ultrasonic cleaner to clean the sample. Then, the sample was in an oven at a temperature of 20-40° to dry, and finally, the sample was ground into a nanocellulose powder that was ready to be characterized.

2.5 Characterization

After the nanocellulose isolation process, the samples were characterized by XRD to determine the crystallite size and crystallinity index and by SEM to determine the morphological structure formed during the nanocellulose manufacturing process.

2.6 Calculation of crystallites and crystallinity index

The crystallite size measurement can be calculated from equation (1) which is formulated by

$$D = \frac{K\lambda}{B\ COS\theta} \tag{1}$$

where D is the size of the crystallite, and K is the form factor of the crystallite. λ is the X-ray wavelength, B is the Full Width at Half Maximum (FWHM), and θ is the diffraction angle (Scherrer,1918). Meanwhile, the crystallinity index can be calculated by equation (2) which is formulated by

$$Crl = \frac{I_{002} - I_{am}}{I_{002}} 100\% \tag{2}$$

where Crl is the value of the crystallinity index, then (I_{002}) is the crystallinity scattering intensity, and (I_{am}) is the amorphous scattering intensity (Segal, 1959).

3. Results and Discussions

3.1 Sample Preparation Results

Sample preparation begins with cleaning the waste of the kepok banana peel with clean water so that it is clean of dirt. Then the kepok banana peel is dried in the sun at 80-90℃ until it dries. Then the banana peel is cut into several pieces until it is ready to be blended until it becomes powder (**Figure 1**).

Figure 1. Sample preparation results

3.2 Nanocellulose Synthesis Results

The results of the production of nanocellulose were obtained through three stages, namely Delignification involving 10% NaOH mixed with 5 grams of kepok banana peel powder, then stirring and allowed to stand for 24 hours until the sample was free from lignin and hemicellulose. Then, the bleaching process uses 10% H_2O_2 mixed with samples free of lignin and hemicellulose and allowed to stand for 24 hours, then washed with distilled water until the color turns white and the pH is neutral. After that, enter the last stage, namely the isolation of nanocellulose, which begins with drying the white cellulose powder at a temperature of 20-40℃ Then the powder is weighed again and mixed with H_2S0_4 solution with various concentrations of 5,10,15, and 20%. Then heated for 3, 5 hours at a temperature of 50℃ and allowed to stand for 24 hours. After that, it was washed with a centrifuge until the pH was neutral, and then the sample was cleaned with an ultrasonic cleaner before being ground into nanocellulose powder and ready to be characterized using XRD and SEM. The results of the three stages can be seen in **Figure 2**.

a b c

Figure 2. Results of all stages of making nanocellulose: (a) Delignification results, (b) bleaching results, (c) Nanocellulose powder

3.3 XRD Characterization Results

3.3.1 Qualitative Analysis

After the nanocellulose isolation stage ended, the samples were characterized by XRD, and the results are shown in **Figure 3**

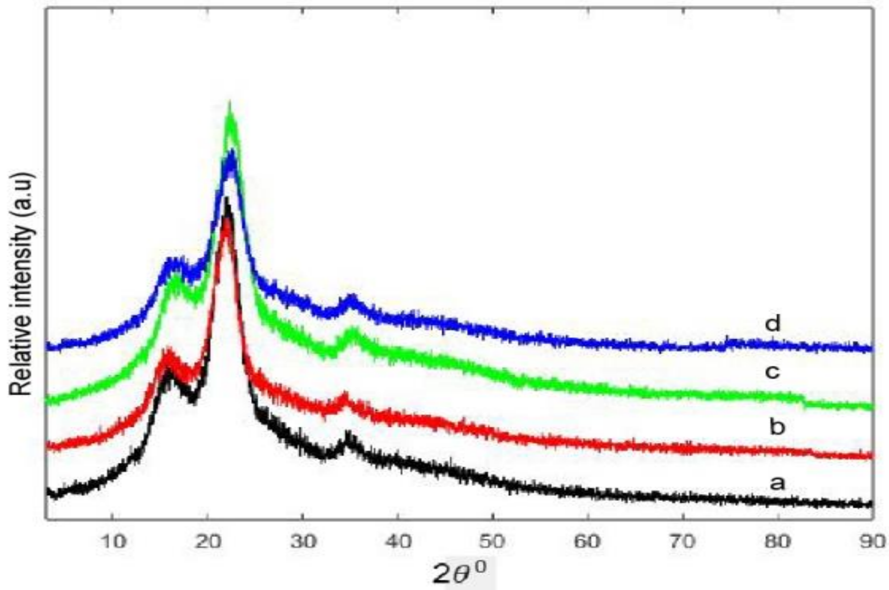


Figure 3. XRD diffractogram of kepok banana peel nanocellulose with variations in H_2SO_4 concentration: (a) 5%, (b) 10%, (c) 15%, and (d) 20%

Based on the XRD diffractogram in **Figure 3**, it can be seen that acid hydrolysis causes the crystalline and amorphous parts to split, leaving a single crystalline part (Eduardo et al., 2015). In the different variations in the existing H_2SO_4 concentrations, it was found that 2Θ respectively 21.86°, 21.92°, 22.30°, and 22.60° with a peak average of 2Θ around 22°, this indicates that the crystal obtained is a crystalline structure of cellulose (Sucaldito & Camacho, 2018). The next step is to calculate the crystallite size using the Scherrer equation [1] and get the results of the crystallite size as shown in **Table 1**.

Table 1. Calculation Result of Nanocellulose Crystallite of Kepok Banana Peel

Concentration (%)	K	λ	*FWHM*(°)	Cos Θ(°)	Nanocellulose Crystal Size (nm)
5%	0.94	0.154	4.21	10.93	1.92
10%	0.94	0.154	4.08	10.96	1.98
15%	0.94	0.154	4.54	11.15	1.78
20%	0.94	0.154	4.72	11.30	1.71

Based on **Table 1**, the size of the nanocellulose crystallites is in the range of 1,71 nm to 1,98 nm. This size is under the size of the CNC in general, which says that the size ranges from < 15-20 nm (Moon et al., 2011). Furthermore, for the crystallinity index calculated by the equation[2], It was found that the crystallinity index as in **Table 2**.

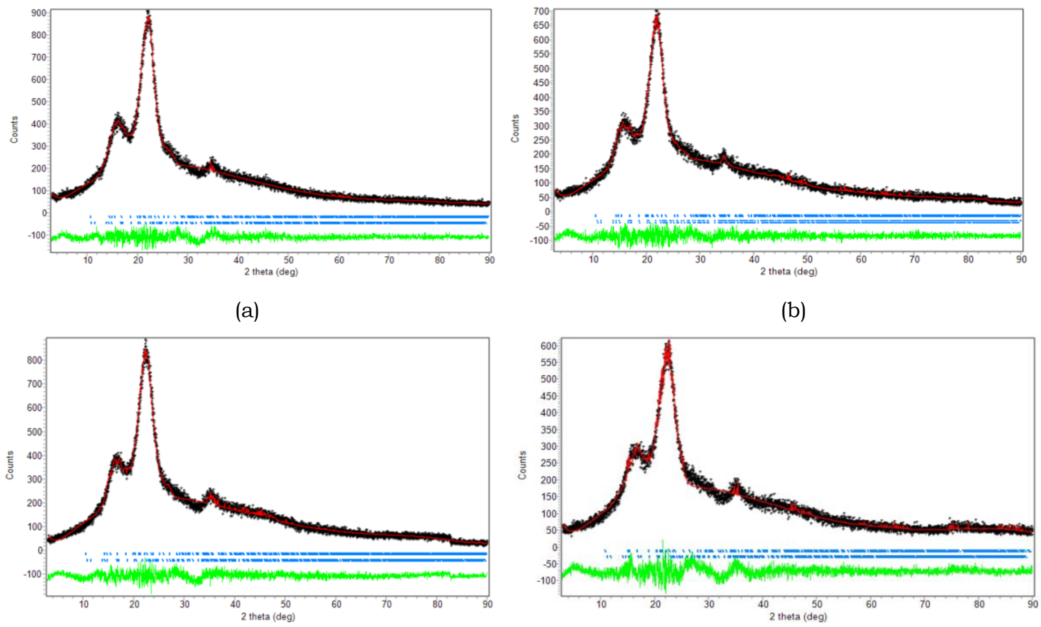
Table 2. Nanocellulose Crystallinity Index

Sulfuric acid concentration (%)	I_{002}	I_{am}	Crystallinity index
5%	889.85	387.03	56.50%
10%	689.20	300.18	56.44%
15%	845.18	368.39	56.41%
20%	617.00	287.00	53.48%

Based on **Table 2**, the size of the crystallinity index ranges from 53.48% to 56.47%, with data having the lowest crystallinity index in sulfuric acid with a concentration of 20%. It is due to the highest acid concentration left overnight that can damage the crystalline structure of cellulose so that the crystalline part is destroyed and dissolved with the amorphous part of the cellulose, which is then wasted with the sulfuric acid solution H_2SO_4. Compared with research conducted by (Ashari et al., 2021) on the same primary material but with different methods, it resulted in a higher crystallinity index of 60.89% to 72.40%. The relative difference in the crystallinity index of CNC can be caused by variations in parameters such as time and concentration, preparation and isolation methods, and even different instruments can also cause differences in the crystallinity index (Jie Gong. 2017).

3.3.2 Quantitative Analysis

Refinement analysis matches measured and calculated data through the Rietica program or the Rietveld method. In this study, the sample has two phases, namely cellulose Iα and Iβ with the standard data for refinement is cellulose Iα the value of a is 6.717 Å, b is 5.962Å, c is 10.400 Å, then the α is 118.08°, the β is 114.80°, and the ϒ is 80.37° and the Z is 1 (Nishiyama et al., 2003). Then cellulose Iβ beta has a value of 7.784 Å, b is 8.201 Å, c is 10.38 Å, ϒ is 96.5°, and Z is 2 (Nishiyama et al., 2002). The results of the refinement of each of these samples can be seen in **Figure 4**.



(c) (d)

Figure 4. The results of the refinement of XRD Nanocellulose banana peel kapok with a concentration of H_2SO_4 (a) 5%, (b) 10%, (c) 15%, (d) 20%

In general, the results of the refinement of each sample have provided a match between the data from the research XRD and the model (red solid). **Tables 3** and **4** below compare the parameters of nanocellulose cells with variations in the concentration of H2SO4 5, 10, 15, and 20% to the model.

Table 3. Parameters of phase Iα Nanocellulose cells

Sample	a (Å)	b(Å)	c(Å)	α (°)	β (°)	ϒ (°)
Model	6.71	5.96	10.40	118.08	114.80	80.37
5%	6.75	6.05	10.66	118.52	116.19	79.04
10%	6.69	6.01	10.52	118.59	115.29	79.77
15%	6.72	6.02	10.57	118.39	115.67	79.27
20%	6.59	6.19	10.47	118.08	113.78	80.41

Table 4. Parameters of phase Iβ Nanocellulose cells

Sample	a (Å)	b(Å)	c(Å)	ϒ (°)
Model	7.78	8.201	10.38	96.50
5%	7.82	8.30	10.51	96.68
10%	7.79	8.27	10.47	96.39
15%	7.80	8.27	1050	96.79
20%	7.87	8.35	10.51	96.55

Tables 3 and **4** show a shift in the Nanocellulose cell parameters against the model. It is because the addition of H_2SO_4 concentration causes the crystallite size to increase, but on the other hand, if the H_2SO_4 concentration is

too high, it can also damage the crystal so that its size decreases. This shift in value also affects the crystallite size, as shown in **Table 1**.

3.4 SEM Characterization Results

Based on the XRD characterization that has been done, the best sample is at a 5% H_2SO_4 concentration. The SEM analysis aims to see the morphology and size of the nanocellulose from the sample with a magnification of 10,000×. The resulting Morphological appearance can look like **Figure 5.**

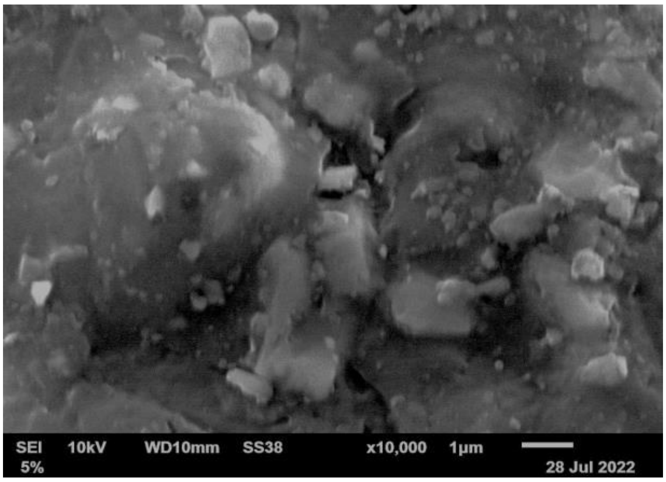


Figure 5. Kepok banana peel nanocellulose morphology

Based on **Figure 5**, it can be seen that the resulting structure is like an irregular lump, and the fibers are not visible, so the size of the nanocellulose cannot be calculated. However (Rosa et al., 2012) have made nanocellulose with coconut pieces using the acid hydrolysis method to produce a more regular morphology and nanocellulose worth 58-515 nm.

4. Conclusions

Based on the research that has been done, the highest crystallite size results are at a 5% H_2SO_4 concentration. The higher concentration can also damage the crystalline structure of cellulose so that the crystalline part is destroyed and dissolved along with the amorphous part of the cellulose, which is then wasted with the sulfuric acid solution H_2SO_4. Meanwhile, the sample's morphology using SEM with a magnification of 10,000× at 5% H_2SO_4 concentration resulted in images such as irregular lumps and no visible fibers.

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