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The Effect of H_2SO_4 Variations on the Synthesis and Characterization of Nanocellulose Using Pineapple Peel Fiber

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Abstract

Manufacturing nanocellulose made from pineapple peel fiber has been carried out using acid hydrolysis. This study aims to determine the effect of variations in H_2SO_4 on the synthesis of nanocellulose in pineapple peel fibers and on the crystal structure, surface morphology, and constituent elements of pineapple skin fiber nanocellulose. The variations of H_2SO_4 used were 5, 10, 15 and 20%. X-ray diffraction (XRD) and Scanning Electron microscopy (SEM) are characterizations used. The results of XRD characterization showed that the size of the resulting crystallite had met the appropriate size in the range of values from 2.03 – 2.21 nm. The results of SEM characterization show that the image is not porous and lumpy.

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Kata kunci: *Kulit nanas, nanoselulosa, hidrolisis asam, H_2SO_4*

Abstract

Pembuatan nanoselulosa berbahan serat kulit nanas telah dilakukan dengan menggunakan hidrolisis asam. Penelitian ini bertujuan untuk mengetahui pengaruh variasi H2SO4 terhadap sintesis nanoselulosa serat kulit nanas dan terhadap struktur kristal, morfologi permukaan, dan unsur penyusun nanoselulosa serat kulit nanas. Variasi H2SO4 yang digunakan adalah 5, 10, 15 dan 20%. Difraksi sinar-X (XRD) dan mikroskop Scanning Electron (SEM) adalah karakterisasi yang digunakan. Hasil karakterisasi XRD menunjukkan bahwa ukuran kristalit yang dihasilkan telah memenuhi ukuran yang sesuai pada rentang nilai 2,03 – 2,21 nm. Hasil karakterisasi SEM menunjukkan bahwa citra tidak porous dan menggumpal.

1. Introduction.

Pineapple is the world's third most important tropical fruit after bananas and oranges—the more. As pineapple production increases, the waste generated also increases. So, the utilization of pineapple peel waste has not been optimal, even though much of it is wasted on the side of the road, disturbing the view. Pineapple skin waste is used only as animal feed (Syauqi & Inasari, 2020). Pineapple skin contains enzymes and cellulose. Cellulose is an organic compound that is the main constituent of plant cell walls. About 33% of all plant matter is cellulose (Klemm, 1998). Cellulose is what can form nanocellulose.

Nanocellulose is cellulose with a diameter of nanometers (2–20 nm) and a length between hundreds to thousands of nanometers, including nanocomposites that are light and have great strength at a reasonably low cost. Nanocellulose in biofilm has poor physical and mechanical properties, namely brittleness, stiffness, and weak tensile strength (Iriani *et al.*, 2015). The synthesis of nanocellulose from -cellulose consisted of four steps: acid hydrolysis, centrifuge, ultrasonication, and freezer drying. In the acid hydrolysis step, -cellulose was added with H_2SO_4 and assisted by a heating process for 5 hours at 50°C while stirring.

This study aimed to determine the morphology and structure of nanocellulose from pineapple peel. Then, the effect of variations in H_2SO_4 was also observed, especially on changes in crystallite size. As a supporter of the analysis, characterization was carried out using XRD and SEM tests.

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2. Research methods

This research was conducted using the acid hydrolysis method, which was carried out with the stages of sample preparation, cellulose isolation, nanocellulose isolation, and characterization, namely XRD and SEM. The tools and materials used are beakers, spatulas, measuring cups, electric stoves, pH paper, plastic wrap, sieve/mesh, oven, aluminum foil, mortar, digital scales, Petri dishes, water bath, tablespoon, basin, centrifuge, magnetic bar, funnel, hot plate, tissue, and filter. Meanwhile, the materials used are NaOH, H_2O_2, aquadest and H_2SO_4.

2.1 Sample Preparation

The first step of sample preparation begins with the pineapple peel, which is cleaned using clean water first, then cut into small parts, then blended again until it becomes pineapple skin powder, ready to be used as the primary material for making nanocellulose. Then, to facilitate the cellulose isolation and bleaching process, the pineapple peel powder was dried in an oven and filtered using a sieve to obtain a finer skin powder. The bleaching treatment is for the bleaching process on the sample. It is done so that the final result of the analysis shows the color of nanocellulose in general. The results of the sample preparation can be seen in **Figure 1**.

Image 1. Sample Preparation Results

2.2 Cellulose Insulation

Cellulose isolation was carried out using 5 grams of pineapple peel waste powder given 10 grams of NaOH solution, and 50 ml of distilled water and stirred using a magnetic stirrer sufficiently, then left for 24 hours with the top condition of the sample solution mixture covered using plastic wrap. The purpose of giving NaOH is to remove impurity components in pineapple peel powder. For the cellulose isolation process, it can be seen in **Figure 2**.

Figure 2. Cellulose insulation results

2.3 Bleaching

For the bleaching process, the pineapple peel powder that has been filtered is mixed with a 10% H_2O_2 solution and then allowed to stand for 24 hours with the top covered using plastic wrap. After being allowed to stand for 24 hours, the H_2O_2 solution was removed and separated from the pineapple peel powder. Then, the filtered pineapple peel powder was washed with warm distilled water until the filtrate turned clear white and the pH was neutral. In this study, approximately 6 washings were carried out to get better results. The purpose of giving H_2O_2 is to get white cellulose and remove lignin and hemicellulose compounds remaining in the fiber to produce a whiter and cleaner product. The bleaching results can be seen in **Figure 3**.

Figure 3. Bleaching Results

2.4 Nanocellulose Insulation

For this nanocellulose isolation process, the acid hydrolysis method was used by drying the powder first in an oven at a temperature of 50°C. After the pineapple peel powder is dry, the following process is to measure the weight of the sample using an analytical balance or scale. In the next step, pineapple peel powder was given a solution of H_2SO_4 and equated with various concentrations of 5, 10, 15, and 20% and then cooked in a water bath for 3.5 hours at a temperature of 500°C, then neutralized using a centrifuge. If the pH is neutral, the pineapple peel solution is filtered again, and the filter results are dried using an oven to get a constant weight. If achieved, the pineapple peel sample can be ground using a mortar to get the desired nanocellulose powder.

Figure 4. Nanocellulose insulation results

2.5. Characterization

At this stage, the nanocellulose skin powder has been characterized using SEM and XRD. The subsequent formula is employed in Equation 1 to ascertain the crystallite size.

$$\boldsymbol{D = \frac{k\lambda}{\beta \cos \theta}} \quad (1)$$

with D as the size of the crystallite, k is the form factor of the crystal (0.9), λ = is the x-ray wavelength (1,54056), β is the value of Full Width at Half Maximum (FWHM) or diffraction peak (rad), θ is the diffraction angle (Scherrer, 1918). In addition to knowing the size of the crystallites, it is also necessary to know the size of the crystallinity index by using the following Equation 2.

$$\boldsymbol{CrI = \frac{I_{002} - I_{am}}{I_{002}} 100\%} \quad (2)$$

with I_{am} as the amorphous scattering intensity and I_{002} as the crystalline scattering intensity is located on the [002] lattice and has a diffraction angle of 2θ about 22° (Segal et al., 1959).

3. Results and Discussion

3.1. XRD Characterization

1. Results of Qualitative Analysis of XRD Nanocellulose. The graph below shows the crystallinity index and crystallite value from equations (1) and (2). A qualitative analysis was conducted using the Rietveld method to gain further insights into cell or lattice parameters. **Figure 5** shows the results of the XRD characterization of pineapple peel nanocellulose from various variations of H_2SO_4. Four peaks characterize cellulose (micro-nano). These peaks include 5, 10, 15, and 20% peaks.

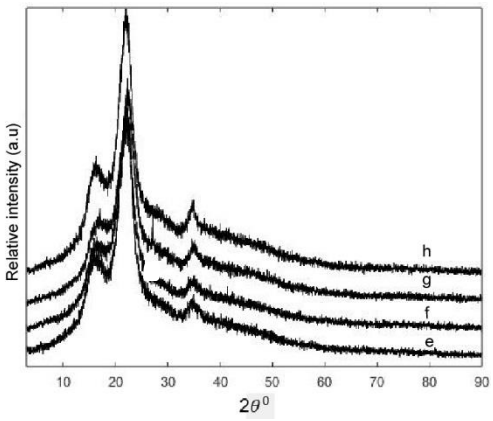

Figure 5. XRD diffractograms for nano cellulose samples 5, 10, 15, and 20%.

From the different variations in the concentration of H_2SO_4, namely 5, 10, 15, and 20%, the diffraction peak was obtained at an angle of 2θ = 22.02˚, 22.14°, 22.20° and 22, 32° then it can be said that the average peak is 2θ its is 22°. Research conducted by Liu et al. (2021) also obtained a peak range of 2θ 15-22°. These peaks represent the crystalline cellulose peaks of the four samples characterized by their sharp diffraction intensity.

2. XRD Nanocellulose Quantitative Results. The first step in finding the highest peak for each sample is changing the XRD test result file from RAW to XY format to refine it into Rietica. Then, the XY format file is inserted into Rietica along with the file containing the phase for nanocellulose and clicked on start and step. The next step is to determine the value of B0, B1, B2, B3, B4, and B-1, then start and step. In order to achieve a smoother image, enhanced peak resolution, and a reduced 2θ value, the values of Iα and Iβ are determined by inputting the parameter values of cell dimensions a, b, and c. In quantitative analysis, standard data is needed; in this case, data from Nishiyama et al. (2003) and Nishiyama et al. are used. (2002) on the crystal structure and hydrogen bonding system in cellulose from synchrotron x-rays and neutron diffraction, the value of lattice parameters, obtained the value of *Ia*, namely a = 6.71700, b = 5.96200, c = 10.40000, λ = 118 .08000, β = 114.80000, γ = 80.37000. As for *Iß*, namely a = 7.78400, b = 8.20100, c = 10.380000, λ = 90.0, β = 90.0, γ = 96.500000. Then, the last step is to determine the value of *Ia* and *Iß* by filling in U, V, and W. After doing these steps, the value will be obtained x^2 below one and a smoother picture. The following refining results are by variations in the concentration of H_2SO_4 used and are presented in Figure 6 using Rietica software, which aims to see the phase and diffraction peaks using the parameters RP, RWP, Rexp, and GOF.

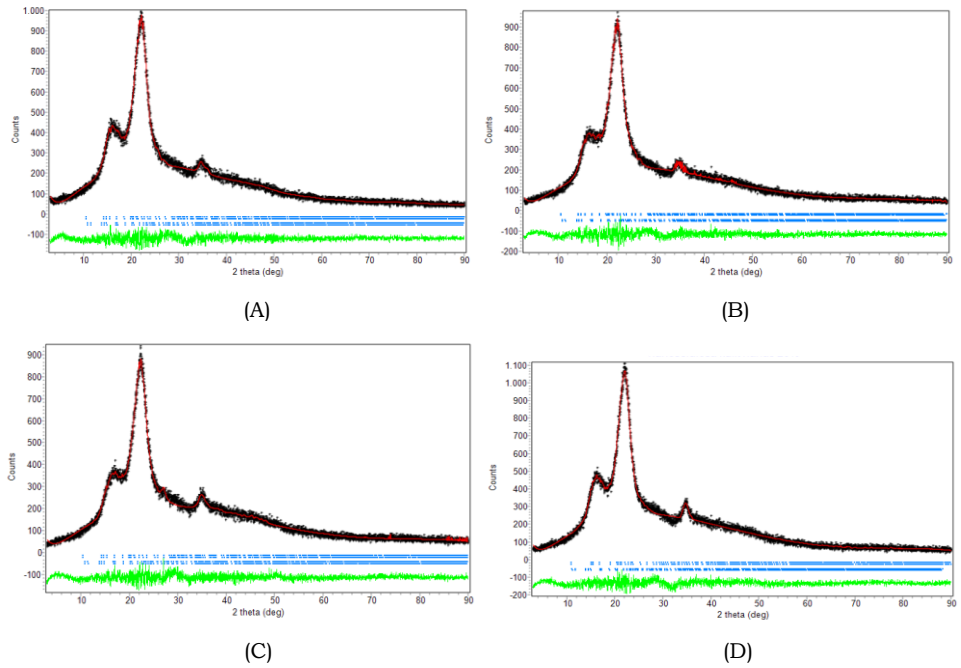

Figure 6. (A) Rietveld refinement of nanocelluloce 5%, (B) Rietveld refinement of nanocelluloce 10%, (C) Rietveld refinement of nanocelluloce 15%, (D) Rietveld refinement of nanocelluloce 20%

After the refinement process, the highest peak was found in the sample with 20% H_2SO_4 concentration. Furthermore, from **Figure 6**, it can be seen that the peaks overlap between the red and black lines. The results of the XRD Nanocellulose quantitative analysis can be seen in **Figure 6**. There are several colors contained in the graph

of the pineapple peel nanocellulose refining, where the red peak is the calculated diffraction pattern (model), the black peak is the measured diffraction pattern, The blue vertical lines are the Bragg peaks belonging to the two identified phases, the green curve is the difference in intensity between the measured and calculated patterns. Then, refining each sample shows a value of 2θ around 22°.

Through the Scherrer equation on the previous page, the nanocellulose crystal size is obtained, as shown in **Table 1**.

Table1. Nanocellulose crystallite size

Sample name (%)	(nm)	*FWHM*(°)	2Θ	Crystallite Size (nm)
5	0.154	4.16	22, 2	4.07
10	0.154	4.07	22.14	4.17
15	0.154	3.37	22.20	4.50
20	0.154	4.01	22.32	4.23

The crystal size results are supported by research conducted by Teixeira et al. (2021) on the absorption of Co+2, which obtained crystallite sizes of 4.1 and 4.7 nm. Then, the crystallinity index is calculated using the Segal formula. The crystallinity index for each sample is obtained in **Table 2**.

Table2. Nanocellulose crystallinity index table

Sample name (%)	I_{002}	I_{am}	Crystallinity Index (%)
5	980. 78	595. 39	39
10	881. 56	507. 70	42
15	943. 57	400.02	57
20	1069. 016	437. 172	59

Based on **Tables 1** and **2**, the size of the crystallinity index ranges from 39% to 59%. It is clear that the acquisition of the crystallinity index value, the higher the level or concentration of H_2SO_4, the greater the crystallinity index. Compared with the results of research conducted by Mittal et al., 2011 it is clear that the highest degree of crystallinity is 78%, and the lowest degree of crystallinity is 43%. In general, the refinement results for each sample have provided a match between the data from the XRD research (black) and the color model (red). XRD data analysis produces an output in the form of improvements to the crystal structure based on the calculated diffraction pattern (model). The following table compares the smoothed cell parameters to the smoothed results of the percentage shift in the measurement value.

Table 3. Parameters of phase *Ia* nanocellulose cells

Sample	*a* (Å)	*b* (Å)	*c* (Å)	*λ* (Å)	*β* (Å)	*γ* (Å)
Model	6,717	5,962	10,400	118.08	114.80	80.37
5%	6.8159	6.0236	10.7109	118.5397	116.5544	79.1755
10%	6.7170	5.9620	10.4000	118.0800	114.8000	80.3700
15%	6.7309	6.1008	10.6657	118.5717	115.4012	79.7065
20%	6.7389	5.9292	10.4506	117.6219	116.1330	79.9427

Table 4. Parameters of phase *Iβ* nanocellulose cells

Sample	*a* (Å)	*b* (Å)	*c* (Å)	*λ* (Å)	*β* (Å)	*γ* (Å)
Model	7,784	8,201	10.38	90	90	96.5
5%	7.8679	8.2999	10.5983	90.000000	90.000000	96.3661
10%	7.7840	8.2010	10.3800	90.000000	90.000000	96.5000
15%	7.8740	8.3516	10.5878	90.000000	90.000000	96.7766
20%	7.7638	8.2353	10.4069	90.000000	90.000000	97.0378

Table 3 and Table 4 reveal alterations in the parameters of phase *Ia* and phase *Iβ*. These modifications are evident when compared to the standard values proposed by Nishiyama et al. Such changes are attributed to introducing H_2SO_4 into the nanocellulose sample, and fluctuations in the concentration of H_2SO_4 are observed to impact the resultant crystallite size outcomes.

3.6. SEM Characterization Results

In order to determine the morphology of various pineapple peel nanocellulose samples, SEM characterization is essential.

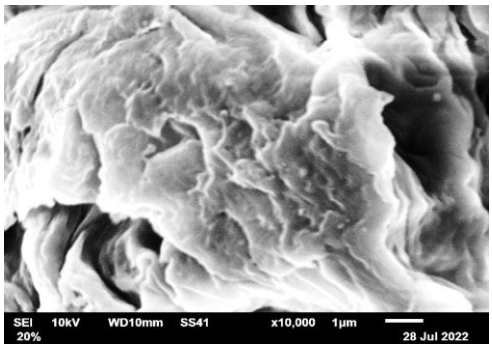

Figure 7. SEM characterization results

Based on the results of the XRD analysis that has been carried out, it was found that the best sample of the four samples studied was at a concentration of 20% sulfuric acid. If we look at the morphological image of pineapple peel nanocellulose, it is in the form of lumps (solid), there are no pores, and it does not show an image of pineapple skin fibers. Compared with the research conducted by Dai et al. (2018) using pineapple peel as the primary material and the same research method, morphological results, such as elongated, porous, and non-clumping threads, were obtained.

4. Conclusions

Based on the research that has been done, it can be concluded that variations in the concentration of H_2SO_4 affect the crystallinity index and particle size, where the higher the concentration of H_2SO_4, the higher the crystallinity index. The greater the concentration of H_2SO_4, the faster the hydrolysis time. The result of the highest nanocellulose crystal size was found in the sample at a concentration of 15% H_2SO_4, with XRD test results obtained at a value of 4.50 nm. Meanwhile, the smallest value obtained was in the 5% sample with a variation of 5% concentration. The value obtained is 4.07 nm. The results of the SEM morphology received were less than the maximum measurements. It resulted in the shape of the size of the nanocellulose SEM in the form of lumps, not porous and not showing fibers.

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