Characterization of cellulose nanocrystalline isolated from banana peduncles using acid hydrolysis

Ratna1,2, S Aprilia2,3,6, N Arahman2,3,4,5,6, A A Munawar1

1Department of Agricultural Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh 23111, Indonesia
2Doctoral Program, School of Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh 23111, Indonesia
3Department of Chemical Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh 23111, Indonesia
4Graduate School of Environmental Management, Universitas Syiah Kuala, Darussalam, Banda Aceh 23111, Indonesia
5Research Center for Environmental and Natural Resources, Universitas Syiah Kuala, Jl. Hamzah Fansuri, No. 4, Darussalam, Banda Aceh 23111, Indonesia
6Atsiri Research Center, Universitas Syiah Kuala, Jl. Syeh A. Rauf, Darussalam, Banda Aceh 23111, Indonesia

*Email: sriaprilia@unsyiah.ac.id

Abstract. The study aimed to characterize cellulose nanocrystalline (NCCs) from banana peduncles using acid hydrolysis. The NCCs isolation process was done by hydrolysis using H2SO4 with concentrations of 1M, 2M, and 3M at a microwave power of 100 Watts within 1 hour of hydrolysis. The product of NCCs was characterized in terms of yield, chemical composition (by FTIR), and its crystallinity. The result showed that the highest yield of 88.33% was obtained in acid hydrolysis at the concentration of 1M H2SO4. The results of the FTIR test showed that non-cellulose content had been removed and demonstrated that the molecular structure of cellulose does not change even when treated at different acid concentrations. X-Ray Diffraction analysis showed that crystallinity decreased by increasing the sulfamic acid concentration. The thermogravimetric analysis confirmed the heat resistance analysis and showed that the NCCs is gradually decomposed at a temperature range of 268.3–415.25 °C. The colour of cellulose nanocrystalline powder darkens as the sulfuric acid concentration increases.

1. Introduction
Banana fibres are the source of nanocellulose, yet, it has not been widely used. Bananas, originating from India to Papua New Guinea, part of the Southeast Asia region, are among the earliest cultivated crops [1]. Several tons of stems, leaves, and fibres are produced during the plantation and processing of bananas, releasing much waste. Therefore, sustainable agricultural practices should be applied to avoid environmental problems. Energy conservation and waste management are some of the challenges faced by many countries. The application of waste technology into usable products will solve waste accumulation [2].
Nanocellulose materials from different plants may differ in physical and chemical properties, such as different dimensions, specific surface area, water dispersibility, and rheological properties [3]. Natural fibres are classified based on their origins, such as animal, mineral, or plant. Plant fibres are further categorized into subgroups according to the sources, such as seed fibre, fruit fibre, leaf fibre, and stem fibre [4]. Plants are a potential source for cellulose production because they are relatively cheap and abundant. Therefore, nanocrystalline cellulose has been approved as the first safe nanomaterial on the Environmental Substances List. It has excellent mechanical properties making it ideal for applications in tissue engineering, and many reports showed it could improve mechanical properties [6]. However, variations in the intrinsic structure in the lignocellulosic material and the isolation method used can affect the size, morphology, and crystallinity of the extracted cellulose nanocrystals [5].

Cellulose is not a completely crystalline structure; it also contains amorphous regions of entangled fibrils forming micropores where penetration of small size molecules, such as water, can occur. Thus, the amorphous phase is considered an important because it can transform into chemical products and biofuels [7]. The basic method for extracting nanocrystalline cellulose from pulp fibres is to remove the amorphous regions of the cellulose, thereby releasing the crystalline part, namely the nanocrystalline cellulose particles. Acid hydrolysis is one method to isolate nanocrystalline cellulose [8], [9]. Acid hydrolysis is a complex heterogeneous reaction consisting of the formation of a conjugate acid, the breakdown of the C-O bond \([\text{C}_6\text{H}_{12}\text{O}_6\text{n}]\), and the liberation of the short-chain [10].

Fibres from plants have been widely used to produce nanocrystalline cellulose through a chemical process called acid hydrolysis. This method not only demonstrates the structural features of nanoparticles in the nanoscale but also exhibits unique strength and optical properties [11]. This study aimed to determine the effect of sulfuric acid concentration on the nanocrystalline cellulose (NCCs) characteristics of banana peduncles. The effect of the treatment will be seen based on the yield analysis, morphological characteristics of Scanning Electron Microscopy (SEM), physical characteristics of X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR), characteristics of heat resistance Thermogravimetric Analysis (TGA) and colour of nanocrystalline cellulose powder.

2. Materials and methods
2.1. Materials
NCCs were isolated from cavendish banana peduncles (Musa acuminata L.), the waste of cavendish banana peduncles obtained from banana traders around Aceh Besar and Banda Aceh, Indonesia. The chemicals used were sulfuric acid 95-97% Emsure®, NaOH Emsure® pellets, H₂O₂ 35% food-grade, and distilled water.

2.2. Hydrolysis nanocrystalline cellulose
Banana peduncles were cut into pieces and pressed using a pressed machine to get the fibre. Next, the resulting fibres were dried and milled. The polymerization process was carried out using 1M NaOH at 450 W microwave, with a temperature around 90 °C for 1 hour. After the polymerization process, the bleaching process was continued using 35% H₂O₂ at 180 W microwave with a temperature around 65 °C for 1 hour. The NCCs isolation process was carried out by hydrolysis using sulfuric acid with concentrations of 1 M, 2 M, and 3 M at 100 W microwave in a temperature range between 45 and 52 °C, with 1 hour of hydrolysis. Once the hydrolysis process was completed, the sample was washed using distilled water until it reached a neutral pH. After that, the sample was centrifuged and ultrasonicated before being dried, mashed, and sieved using a 500 mesh sieve. Then analysis was carried out in the form of yield, characterization of NCCs with FTIR, XRD, TGA, and colour.

2.3. Characterization of nanocrystalline cellulose
2.3.1. Yield Percentage. The final sample weight (Ma) and initial weight (Mi) were measured to calculate the yield. The yield is determined using the following equation [12].
Yield (%) = \frac{M_a}{M_i} \quad (1)

2.3.2. X-ray diffraction. The crystallinity index (CI) was calculated based on the deconvolution method as follows.

\[ CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2) \]

Where \( I_{002} \) is the highest peak intensity for the crystal region and \( I_{am} \) is the minimum peak intensity for the amorphous region \([13],[14]\). The crystal size was calculated using the Scherrer formula as given in Equation (3).

\[ D = \frac{K\lambda}{\beta^{\frac{1}{2}} \cos\Theta} \quad (3) \]

Where \( K (0.91) \) is Scherrer's constant, and \( 1/2 \) is the full width at half maximum (FWHM) and \( \Theta \) is the Bragg angle \([15]\).

2.3.3. Fourier transform infrared spectroscopy. Fourier transform infrared spectroscopy (FTIR) analysis was undertaken using Shimadzu IRPrestige 21 FTIR spectroscopy in a wavelength range of 4000 - 400 cm\(^{-1}\).

3. Results and discussion

3.1. Yield percentage

The NCCs produced from the isolation of sulfuric acid parameters (1 M, 2 M, and 3 M) for a 1-hour process ranged from 88.3–72%, as shown in Figure 1. The highest NCCs produced were in the 1 M \( \text{H}_2\text{SO}_4 \) hydrolysis treatment (88.3%), and the lowest was in the 3 M \( \text{H}_2\text{SO}_4 \) treatment (72%).

\[ \text{Figure 1. The yield of NCCs isolated from banana peduncles} \]
It shows that the higher the concentration of H2SO4 the lower the NCCs produced. The hydrolysis process of NCCs using a high concentration of acid enhanced the hydrolysis process, resulting in more soluble glucose monomers during washing and reducing the yield of cellulose produced [17].

3.2. Fourier transform infrared spectroscopy

Figure 2 displays the results of the FTIR NCCs spectrum from banana peduncles with acid hydrolysis treatment influenced by H2SO4 concentrations of 1 M, 2 M, and 3 M. The largest spectrum was shown in the absorption region of 3200 - 4000 cm⁻¹ (O-H stretching). The spectra of the three concentrations of H2SO4 (1 M, 2 M, and 3 M) showed the same absorption region of 3200-4000 cm⁻¹, namely 3294.42 cm⁻¹, 3331.07 cm⁻¹, and 3332.99 cm⁻¹. The higher the concentration of H2SO4 the greater the absorption. The absorption region of 2500–3000 cm⁻¹ was related to C-H stretching. The absorption region spectrum of 2900 cm⁻¹ of C-H stretching on the CH₂ was from the CH₂-OH group of cellulose [18].

The absorption region of 500-1500 cm⁻¹ was associated with C-O. The acid hydrolysis reaction process on cellulose was conducted using sulfuric acid diluted with water to form H₃O⁺ ions. The H⁺ ions then reacted with one of the cellulose rings to form O-H bonds. This reaction produces H₂O, which then will react with the other cellulose ring to form an O-H bond and creates H⁺ ions [18]. NCCs from banana peduncles increased in O-H with the increasing H₂SO₄ concentration, indicating the greater absorption.

3.3. Thermogravimetric analysis

The thermogravimetric analysis measured the thermal stability of NCCs of banana peduncles hydrolysis using H₂SO₄ of 1 M, 2 M and 3 M. Figure 3 shows the initial weight loss of NCCs from banana peduncles
hydrolysis at the three concentrations in region 2 with a temperature range due to volatile compounds and water molecules evaporate. In regions 3 and 4, cellulose decomposition occurred at a temperature of 268.3–415.25 °C. The loss of weight in the temperature range of 75–125 °C due to volatile compounds and water molecules that evaporate and above a temperature of 200 °C will occur decomposition (degradation) of cellulose [9]. Region 4 shows the mass of NCCs until it reaches a temperature of 600 °C. The residues produced for the concentration of H$_2$SO$_4$ 1 M, H$_2$SO$_4$ 2 M, and H$_2$SO$_4$ 3 M were 12.57 %, 17.48 %, and 10.86 %, with a weight loss of 87.43%, 82.52%, and 89.14%.

![Thermogravimetric analysis NCCs from banana bunches](image)

**Figure 3.** Thermogravimetric analysis NCCs from banana bunches

Thermal decomposition increased with the length of the process and the change in weight loss significantly decreased during the process. This phenomenon could occur due to the increase in the thermal stability of NCCs. NCCs showed a more dense and compact structure after successive removal of the amorphous moiety [19].

### 3.4. X-ray diffraction

The X-ray diffraction (XRD) pattern of NCCs from banana peduncles can be seen in Figure 4. The XRD diffraction peaked at 2θ for the concentrations of 1 M, 2 M, and 3 M H$_2$SO$_4$ (22.2°, 22.29°, and 22.19°). All diffraction patterns peaked at 2θ around 22, indicating type I crystal structure of the cellulose for all samples. The diffraction peaks at 16.4°, 22.5°, and 34.4° corresponded to the planes of the typical β cellulose structure. Hydrolysis of cellulose by sulfuric acid is included in multiphase hydrolysis. The hydrolysis process occurs between solid-phase cellulose and sulfuric acid solution to maintain the cellulose structure. At the start of hydrolysis, H$^+$ attacks the amorphous region, with a rapid decrease in the degree of polymerization (DP) upon cleavage of the long-chain glucose. Furthermore, hydrolysis occurs on the microcrystalline surface, breaking the microcrystals into smaller crystals [20].
4. Conclusions
The highest yield was obtained from the isolation of NCCs using the acid method at a concentration of 1 M H₂SO₄ (88.33%). The highest absorption spectrum in the FTIR test was at a concentration of 3 M H₂SO₄ (3332.99 cm⁻¹). Furthermore, all samples showed a diffraction pattern around 22 at 2θ, indicating cellulose I. The highest crystallinity was obtained at a concentration of 1 M H₂SO₄ (58.93%). All treatment concentrations of H₂SO₄ crystal size were on the nanometer scale and the largest sample weight loss occurred at a concentration of 3 M H₂SO₄ (10.86%).

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Figure 4. X-ray diffraction pattern of NCCs from banana peduncles
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