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Characteristics of Cellulose Nanofibrils From Arabica Coffee Skin Prepared by the Acid Hydrolysis

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Abstract. Cellulosenanofibrils (CNF) is a new generation material that has high performance, good physics and medical properties and is a renewable material that has been developed from various sources using the acid hydrolysis method. CNF synthesis is generally obtained from logs that have a high amount of cellulose fiber. Cellulose nanofibrils (CNF) from arabica coffee skins have great potential to be developed as raw materials for medicines, which function as wound healing agents, surgical sutures, diet medicines, and skin softeners. CNF is produced from Arabica coffee skin through delignification, namely the removal of lignin and hemicellulose by extraction with alkali until α-cellulose is obtained, then CNF is synthesized through hydrolysis using dilute acid. From the coffee skin extraction results, a high cellulose yield was obtained, reaching above 24.30% and crystallinity reaching 79.60%. Hydrolysis by 10%, 12% and 15% HCl with a reaction time of 2 hours, the respective crystallinity was 80.66; 79.06; and 77.69%.

Keywords: CNF, coffee skin, extraction, acid hydrolysis

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INTRODUCTION

Nanocelluloseis a new generation of materials that have the potential to be used in modern society because they have good mechanical properties and from renewableresources [1]. Nanocellulose has an interesting structural behavior, in combination with high specific strength and rigidity so that the engineering of mechanical and optical properties continues to be developed. Cellulose nanoparticles are divided into cellulose nanocrystals and cellulose nanofibrils (CNFs) [2]. Nanocellulose are molecules that contain well-organized atomic structure, nano-size, highcrystallinity, and also don't have amorphous region [3]. CNF is generally obtained from higher plants such as wood, cotton, coconut fiber, wheat straw, bamboo fiber, kenaf, hemp fiber, and coffe skin and husk. In addition,

Nanocellulose is also produced from tunicate and bacterial cellulose as a source of cellulose [4].

However, the use of traditional fiber sources such as wood and bamboo has several limitations. First, cutting down forests to obtain wood can cause deforestation and environmental damage. Second, bamboo takes a long time to grow and reach maturity, so CNF production from bamboo is less sustainable. Third, the process of extracting fiber from wood and bamboo is often complicated and requires a lot of energy. On the other hand, Arabica coffee skins are an abundant source of fiber and have not been utilized optimally. This waste is generated in large quantities from the coffee processing industry, and is generally thrown into landfills or burned, which can cause environmental pollution.

Coffee skin contains 55-65% cellulose, 35% lignin and other impurities [5]. Therefore, the use of coffee skins as an innovative nano cellulose product needs to be developed as a superior product in the biomedical field. According to Putri, A. P et al., (2022), coffee skin waste consists of 63% cellulose, 23% hemicellulose and 17% lignin, 11.5% protein, 1.8 – 8.56% tannin and 6.5% pectin [6]. The main constituent component of Arabica coffee skin waste is cellulose which has the potential to be synthesized into CNF [7]

CNF is generally synthesized using a sulfuric acid catalyst through a two-step process, initial hydrolysis to decompose the amorphous regions of the cellulose polymer and subsequent fragmentation of the crystal segments (mechanical, sonication, etc.) to produce nanocrystals [8]. Unfortunately, this method has several weaknesses, including many cellulose crystals being degraded so that the crystal yield obtained is less than 35% and the resulting product shows low thermal stability with a Tmax of 250 ^{o}C [9]. The use of high concentrations of strong acids has the disadvantage that apart from leaving an acid catalyst that is not environmentally friendly, the yield obtained is also low because the nanocellulose crystal chains are degraded into glucose. Several low concentration organic minerals such as maleic acid through ultrasonic and hydrothermal processes can be applied to synthesize CNF, but the yield obtained is still very small because maleic acid is unable to fragment crystal segments to obtain nano-sized crystals [9][10].

Several previous studies carried out the manufacture of nanocellulose, including Moran et al. carried out the preparation of nanocellulose by hydrolysis using 60% H_2SO_4 at a temperature of 45^{o}C with continuous stirring, the cellulose nanocrystals obtained were white crystals with a crystallinity index of 72, particle size 9.1 nm [11]. Yu et al., (2013) carried out hydrolysis of cellulose into cellulose nanocrystals using acid to obtain a crystallinity of 88.6% and the degradation temperature reached (T_0) 322.5^{o}C[12]. The hydrolytic reaction is limited by a relatively short reaction time so that the acid can only degrade the amorphous areas in cellulose.

The process of synthesizing cellulose nanocrystals is carried out through hydrolysis of cellulose using dilute hydrochloric acid under combined conditions with a hydrothermal sonication process at a temperature of 110^{o}C, and crystallinity that reaches 79% and a crystallite size below 10 nm can be obtained [13]. Based on the characterization of cellulose obtained from coffee husk waste, a crystallinity of 82.47% was obtained. This has the potential to be synthesized into nanocellulose which can be applied as a raw material for medicine [14]. In the research of Kumar et al., (2014) they developed a nanofiber membrane from coffee skin waste using the TEMPO (2,2,6,6–tetramethylpiperidine–1–oxyl) oxidation reaction technique (SN Kumar in 2024. CNF membrane obtained with a thickness of 10-25 µm. [15]

Therefore, this research aims to explore the potential of Arabica coffee skins as an alternative source for CNF production. This research will focus on developing an efficient and environmentally friendly hydrolysis method using low concentration hydrochloric acid. Then the resulting CNF is characterized to determine the chemical structure, crystal structure, morphology and thermal properties.

METHODOLOGY

Material

Coffee skin are biomass residu, was taken from coffe rosting plant. Coffee skin was extraction by 3,5% HNO_3 and 10 mg $NaNO_2$, and digestion by 2% NaOH and 2% Na_2SO_3 from Merck, and 1,7% NaOCl and 10% H_2O_2 from PT. Bratachem. Acid solution for hydrolysis is HCl from Merck. Aquadest that was used for washing the sample from PT. Bratachem.

Intrumentations

Autoclave for hydrolysis, Fourier transform infrared (FT-IR) spectrophotometer Nicolet 8700, scanning electronic microscopy (SEM) models Oxford INCA 400 voltage 15 KV, X-ray difraction (X-RD) type Philips PZ1200, thermogravimetric analyzer (TGA) type NETZSCH TG 209 F1.

Extraction of α-Cellulose from Arabica Coffee Skin

50 grams of Arabica coffee skins were mixed in 1 liter of a mixture of 3.5% HNO_3 and 10 mg $NaNO_2$, heated on a hot plate at 75°C, 90°C, and 100°C for 2 hours. The Cellulose Extract obtained was washed until neutral. The digestion process with 2% NaOH and 2% Na_2SO_3 solution aims to convert the Cellulose chain into α-Cellulose. Then filtered and the dregs washed until neutral. Next, bleaching was carried out with 250 ml of 1.75% NaOCl solution at boiling temperature for 0.5 hour. Then filtered and the dregs washed until the pH of the filtrate is neutral. Followed by bleaching with 10% H_2O_2 at 60ºC in the oven for 1 hour. Then stored in a desiccator.

Cellulose Nanocrystals Synthesisand Characterization

To obtain nanocellulose, α-Cellulose was hydrolyzed with (HCl 10; 12; 15) % at a temperature of 45°C for 1 and 2 hour. Then cooled and added with 125 mL of aquabidest, then left overnight until a suspension was formed. The suspension formed was centrifuged at 10,000 rpm for 20 minutes until the pH was neutral, then placed in a dialysis membrane and immersed in 100 ml of aquabidest, left for 4 days while stirring. Then the aquabidest was evaporated at a temperature of 70°C to obtain cellulose nanocrystals. Then the same treatment was carried out at varying hydrolysis times of 2 hours, 4 hours and 8 hours. After CNC obtained characterized by FT-IR, SEM, X-Rd and TGA.

The crystallinity of the cellulose and CNF samples was determined by Segal's method:

$$Crl = \frac{\mathrm{I}(crystaline) - \mathrm{I}(amorf)}{\mathrm{I}(crystaline)}\ 100\ \% \quad \text{..... (1)}$$

Where $\mathrm{I}_{(\text{cristaline})}$ is the intensity in the crystalline region. This region is indicated by high intensity at angle 2θ, namely at 22º and 23º. $\mathrm{I}_{(\text{amorf})}$ indicated with a minimum intensity that is at 2θ between 18 º and 19 º. θrelates to Brag's law regarding the angle of incidence and departure of light after interacting with the material. Crystallite sizes were estimated from 110, 110, and 200 lattices planes in cellulose by the well-known Scherrer equation:

$$D_{hkl} = \frac{K.\lambda}{\mathrm{B}hkl\ .\cos\theta} \quad \text{..... (2)}$$

Where D_{hkl} is the crystal size in the direction normal to the hkl family in the latice plane. *K* is the Scherrer constant (1.00 for equatorial reflections of rod-like or needlelike crystallites). λ is the wavelength of the radiation (1.54 Aº), and Bhkl is the full width at half-maximum (FWHMLeft) in radians of the reflection of that family of lattice planes. The crystallinity of cellulose using the X-RD test can be seen in Figure 4.

RESULTS AND DISCUSSION

Cellulose from Arabica Coffee Skin Waste

Cellulose obtained from Arabica coffee skin waste is shown in Figure 1. The isolation process was carried out with 3.5% HNO_3 and 10 mg $NaNO_2$ at a temperature of 75ºC, 90ºC, and 100ºC for 2 hours, showing that the higher the extraction temperature, the cellulose yield increased, from 21.0% to 47.9%. The graph of yield increase against extraction temperature is shown in Fig.2.

Fig. 1a Fig. 1b Fig. 1c

Figure 1. Difference Arabica Coffee Skin and cellulose; (a) Coffee Skin, (b) cellulose, (c) cellulose nanofiber

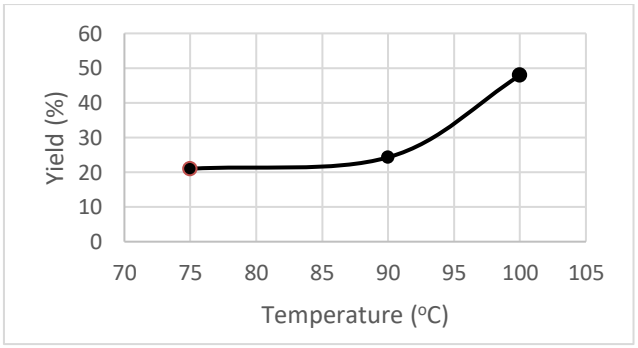

Figure 2.Yield of Cellulose obtained by extraction Temperature of 75ºC, 90ºC, and 100ºC.

Cellulose does not dissolve easily in alkali while lignin and hemicellulose dissolve easily in alkali at low concentrations. If the temperature is too high, it causes cellulose to be degraded along with lignin and hemicellulose, so that the temperature is maintained at the right condition. As shown in Figure 2 at a temperature of 100 ºC, it is believed that lignin is completely dissolved with alkali so that cellulose is easily separated from cellulose.

The higher the extraction temperature indicates the higher the yield obtained. This is because temperature plays a very important role in separating lignin and hemicellulose. At an extraction temperature of 100 ºC, a very significant increase in yield was seen, this was because at a temperature of 100 ºC NaOH was able to dissolve all the lignin, causing the cellulose yield to be higher, whereas at temperatures of 70 and 90 ºC NaOH was not able to dissolve and degrade lignin properly so the yield did not increase sharply. According to Fatimah et al., the higher the temperature used, the more cellulose will be released (Fatimah et al. 2018).

Cellulose Nanofibril Preparation Conditions

The results of characteristics of cellulose nanofibril (CNF) from Cellulose based Arabica Coffee Skin under hyrdrolysis conditions for 45°C wassummerizesd at table 1.

Table 1. Nanocellulose hydrolysis results (5 grams of cellulose)

Time of hydrolysis (hour)	**Concentration of HCl**	**Mass of raw material** (gr)	**Mass Product** (gr)	**Product Color**	**Yield** (%)	**Crystallinity (%)**
1 hour	8%	5	4.7919	A little yellow	95.84	78.27
	10%	5	2.5051	White	50.10	79.66
	12%	5	2.0028	White	40.06	78.06
	15%	5	20138	White	40.28	76.69
2hour	8%	5	3.7919	White	80.84	77.27
	10%	5	3.4510	White	67.10	80.66
	12%	5	2.8028	White	60.06	79.06
	15%	5	2.3138	White	50.28	77.69

Table 1 shows the yield and crystallinity obtained from CNF, where at a reaction time of 1 hour with a heating temperature of 45oC and hydrolyzed with 8% HCl, 4.79 grams of cellulose nanocrystals were obtained with a yield percentage reaching 95.84% and a crystallinity of 78.27%. Meanwhile, at a reaction time of 2 hours at a temperature of 45ºC, when hydrolyzed with 8% HCl, 3.79 grams of cellulose nanocrystals were obtained with a yield percentage of 80.84% and a crystallinity of 77.27%. Then, under hydrolysis conditions with HCl concentrations of 10%, 12% and 15% at a temperature of 45ºC, CNF crystallinity was obtained at 80.66%, 79.06% and 79.06%, respectively.

Hydrolysis of cellulose using 10%, 12% and 15% hydrochloric acid shown a white suspension. High concentrations of hydrochloric acid can excessive degradation of the cellulose chains. In addition, the high concentration of hydrochloric acid is quickly penetration between one layer of cellulose and breaks the hydrogen chains in the amorphous region, leaving a crystalline cellulose region. The decrease in yield is due to the longer reaction time,so the crystalline region in cellulose to be degraded and causes carbonization which is indicated by a black suspension color.

The table 1 shown degradation has occurred to be glucose at the reaction time of 2 hours due to long reaction time. Reaction time can affect CNF forming, the longer the reaction time the hydrolysis causes the faster CNF to be degraded into glucose. So the limitation of reaction time needs to be considered.

Chemical Structure Analysis of Cellulose

The characteristic feature of the FT-IR spectrum of cellulose is that it displays two main absorption areas, namely in the high wave number and low wave number areas as shown fig 3. From the test results of cellulose from Arabica coffee skin, it was found that the high wave number was 2800-3300 $cm^{-1}$and the low wave number was 500-1400 cm^{-1}. The spectrum shows a broad absorption peak located at 2800-4000 cm^{-1} which is a stretch of the –OH group. The absorption peak in the 2890-2900 cm^{-1} area is related to the -CH_2 group, this is in accordance with research conducted by Jahan et al. [15]. The absorption peak in the 2844 cm^{-1} area is an overlap of the -CH_2 band.

The functional group analysis of cellulose using the FT-IR test resulting from extraction with 2%NaOH at a temperature of 40ºC can be seen in Figure 3.

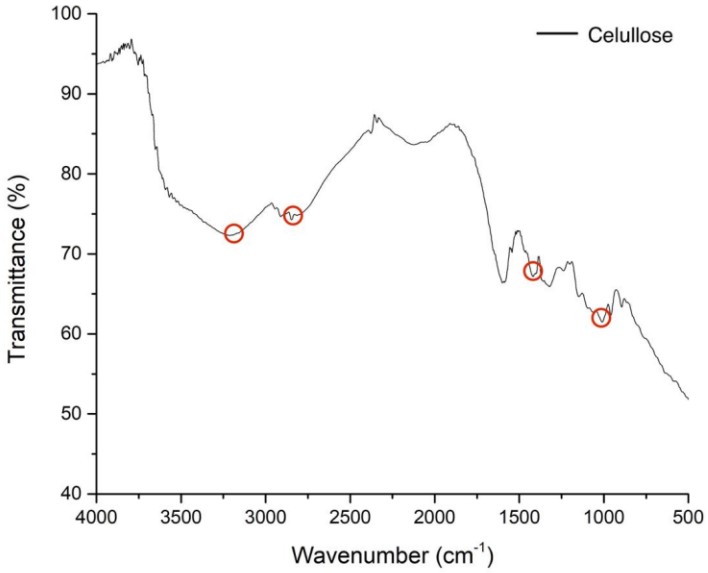

Figure 3. FT-IR spectrum of cellulose extracted with 2% NaOH at a temperature of 90ºC.

Figure 3. for cellulose shows an increase in intensity in the 1050 cm^{-1} band which indicates stretching of the C-O-C pyranose ring, this implies that there has been an increase in the value of cellulose crystals [16]. The absorption peak in the 400 cm^{-1} region is the lowest C-H vibration of cellulose (anomericvibration, specific for β-glucosides) [17]. So the spectrum corresponds to the cellulose group which has the –OH, C-H, and C-O-C absorption peak groups.

Chemical structure of CNF

The spectrum shows that the –OH group absorption peak is located at 3300 - 3400 cm^{-1} and the -CH2 group absorption peak is located in the 2890-2900 cm^{-1} area, which is a typical peak for CNF. The CNF spectrum apart from Figure 4 does not show an absorption peak at 1454 cm^{-1} which is the bending vibration region of O-C-H originating from the lignin component, this is in accordance with what was described by Yu et al. (2013)[12], the absence of this absorption peak indicates that CNF has completely removed lignin. The absorption peak that appears in the 1300-1365 cm-1 region in all spectra is the vibration band of C-H and C-O which related to the aromatic ring of the polysaccharide.

Compared with cellulose, CNF shows a sharp intensity in the 1050 cm^{-1} band indicating C-O-C stretching of the pyranose ring, according to Correa et al. (2010)[16], this indicates that there has been an increase in the value of cellulose crystals. Overall, all the CNF spectra in Figure 3 show the same characteristics, where all the spectra have the same absorption peaks and many peaks have disappeared, indicating that the absorption bands in the lignin region and amorphous cellulose chains have disappeared. The results of the analysis of the crystal structure of cellulose nanocrystals using the FTIR test which were hydrolyzed with HCl (10, 12, 15) % at a reaction time of 1 hour at a temperature of 45ºC can be seen in Figure 4.

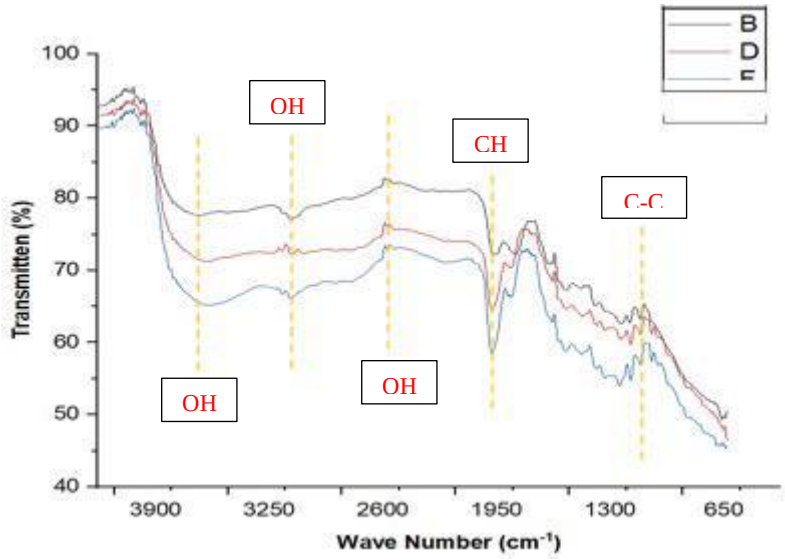

Figure 4. Typical of FT-IR spectra from CNF obtained through hydrolysis using 10%, 12%, 15% HCl and reaction time of 1 hours at 45 °C.

The difference between the spectra of cellulose in fig. 3 and CNF is shown in Figure 4. The wide absorption peak areas at 3500, 3334, and 3280 in cellulose indicate free O-H vibrations from a group of hydroxyls in the cellulose molecule, peak areas at 1950 in cellulose indicate free C-H These peaks show clear differences in the CNF spectrum. The spectrum of cellulose and CNF also shows a peak that appears at 895 cm^{-1}. This peak is the stretching of the glucose ring which is a change in the C-C form in cellulose and hemicellulose.

Cellulose Crystals Structure Analysis

The results of the analysis of the crystal structure of cellulose using the X-RD test extracted with 2% NaOH at a temperature of 100 ºC can be seen in Figure 5.

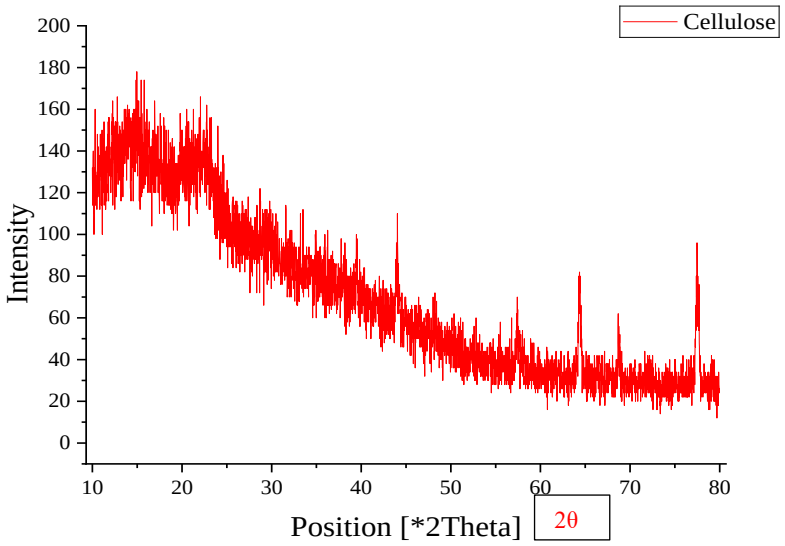

Figure 5. Typical of X-ray diffraction from cellulose obtained through extraction with 2% NaOH, time of 2 hours at 100 °C.

The X-RD pattern in Figure 5 shows a high peak appearing at an angle of 2θ around 22.5º, this area is a typical peak of the cellulose structure [18]. All diffraction patterns for the cellulose crystal plane show 2θ peaks around = 16 º, 22 º and 35º, the minimum diffraction pattern for the

amorphous plane shows 2θ around = 18 º and 19 º. According to Rosli, the characteristic peak of cellulose crystals is at an angle of 22º -23º[19]. The crystallinity of cellulose obtained through hydrolysis using 2% NaOH at a temperature of 100 ºC is 72.60%. The high crystallinity obtained is due to the removal of hemicellulose and lignin in the amorphous area which leads to the arrangement of the cellulose molecules [17].

CNF Crystals Structure Analysis

The analysis of the crystal structure of CNF by hydrolyzed using HCl (10, 12, 15)% and reaction times of 1hour at a temperature of 45ºC shown in Figure 6. Resulted of analysis shown that nanocellulose product from Arabica coffee skin has crystallinity can be used as a medical raw material.

All CNFs show a maximum crystal diffraction peak located at an angle of 2θ = 22 º -23 º with the 002 lattice plane, this shows that the crystals obtained are cellulose I. This indicates that hydrochloric acid is able to maintain the crystal region which is at a weak peak angle. Figure 6 shows a crystallography of the relationship between crystallinity and reaction time.

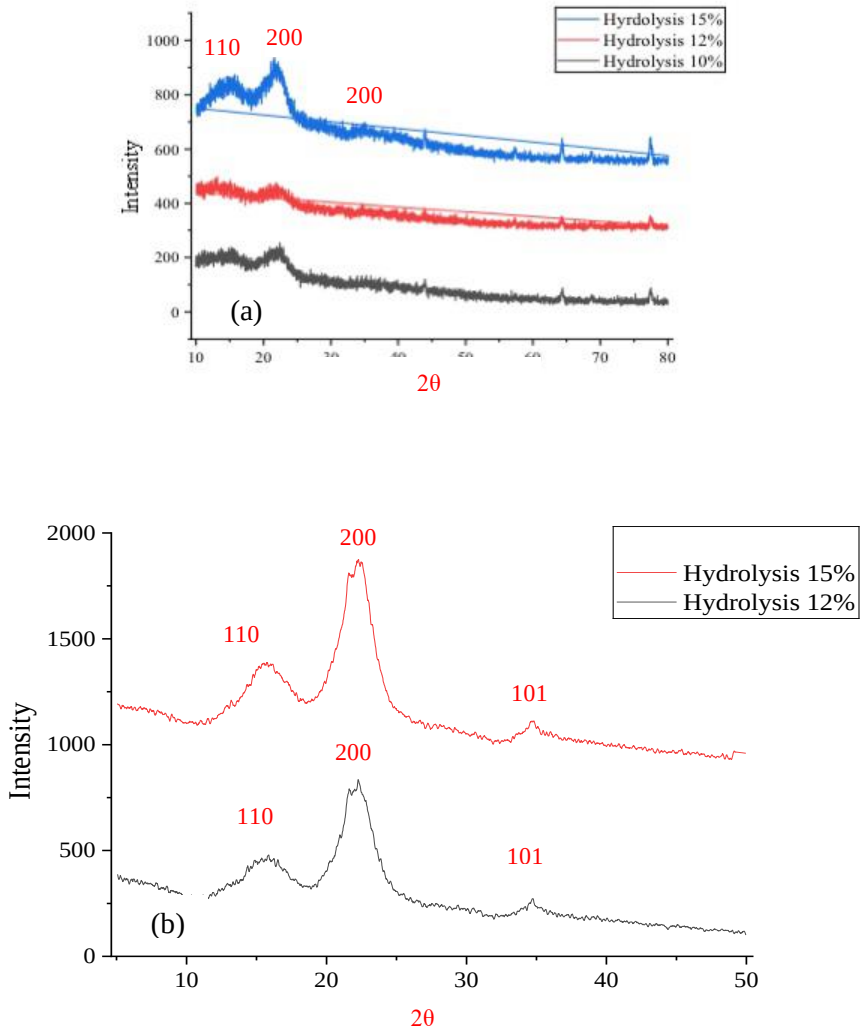

Figure 6. X-RD pattern (a) CNF hydrolysis use (10, 12, 15) % hydrochloride acid and reaction time 1 hour (b) CNF hydrolysis use (12, 15) % hydrochloride acid and reaction time 2 hour

All CNF showed high crystallinity which can be achieved at reaction times of 1 hour with 10% hydrochloride acid obtained crystallinities of 79.66% and 80.66% is obtained, and at a reaction time of 2 hours with 12% hydrochloric acid a crystallinity of 46,6%, while 15% hydrochloric acid

abotained a crystallinity of 24,16%. This is shown treatment acid catalyst with reaction time 1 hour has maximal into cracking of cellulose chain to be more short, where acid can easily attack the amorphous region and leave the crystalline, then fractionated into nanocrystal size.

The use of an HCl concentration of 15 showed clearer results because it triggered more effective acid hydrolysis of the cellulose structure of Arabica coffee skin waste. This allows the optimal release of acetyl and hemicellulose groups, resulting in purer and more structured nanocellulose fibers. This results in higher crystallinity and smaller crystal size. Therefore, a HCl concentration of 15% is more suitable for medicinal raw material applications.

Morphological characteristics

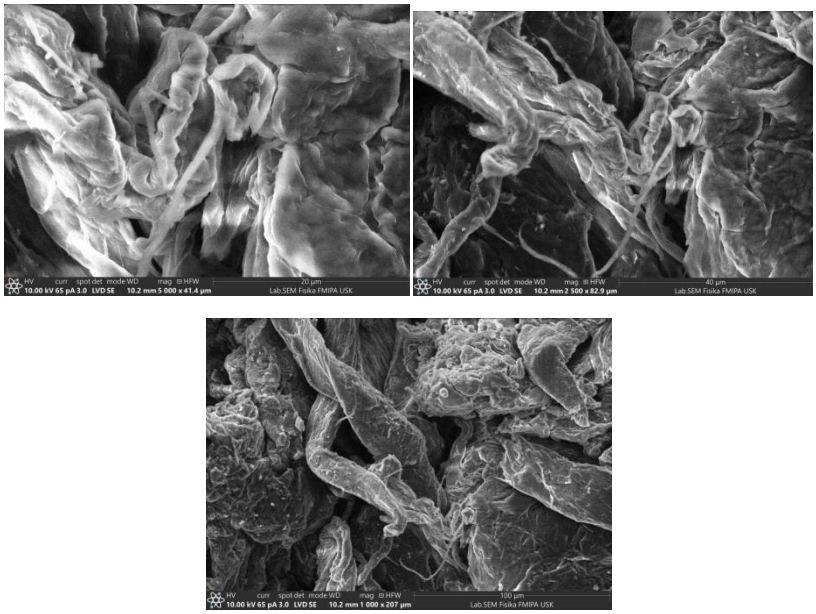

Figure 7. SEM image of arabica coffee skin cellulose

Figure 7 of the coffee skin cellulose reveals a material structure with intricate morphology and porosity. Its surface appears rough and uneven, riddled with pores. This characteristic structure is a hallmark of cellulose, indicating its high porosity and extensive surface area. Coffee skin cellulose holds immense potential for various applications, including biomaterials and composite materials.

Figure 9 shows the surface morphology of nanocellulose crystals. Scanning electron micrographs (SEM) can provide an image of the resulting CNF in the form of a fine fiber structure with dimensions of 5 µm. Reaction time, temperature and the nature of the raw material greatly determine the yield and particle size distribution [18]. The CNF obtained showed a small particle size, this proves that the cellulose chains can be broken into individual crystals by hydrochloric acid hydrolysis and the crystal region can withstand acid attack so that it only breaks the amorphous part, then fragmentation of the crystal segments into nano-sized particles as in figure 8.

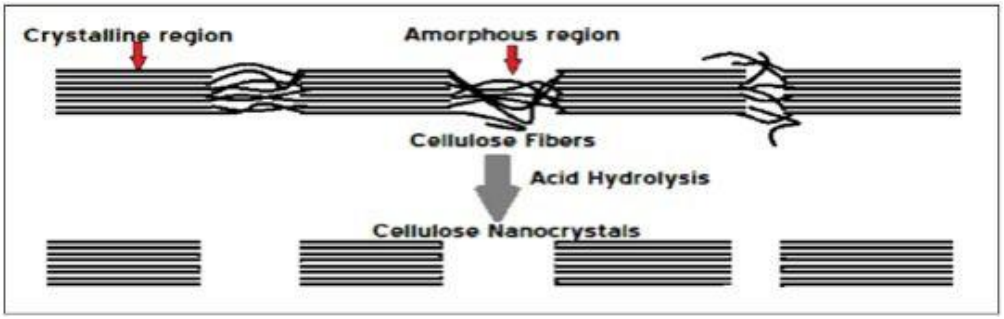

Figure 8. Cleavage of amorphous cellulose chains and formation of individual nanocrystals

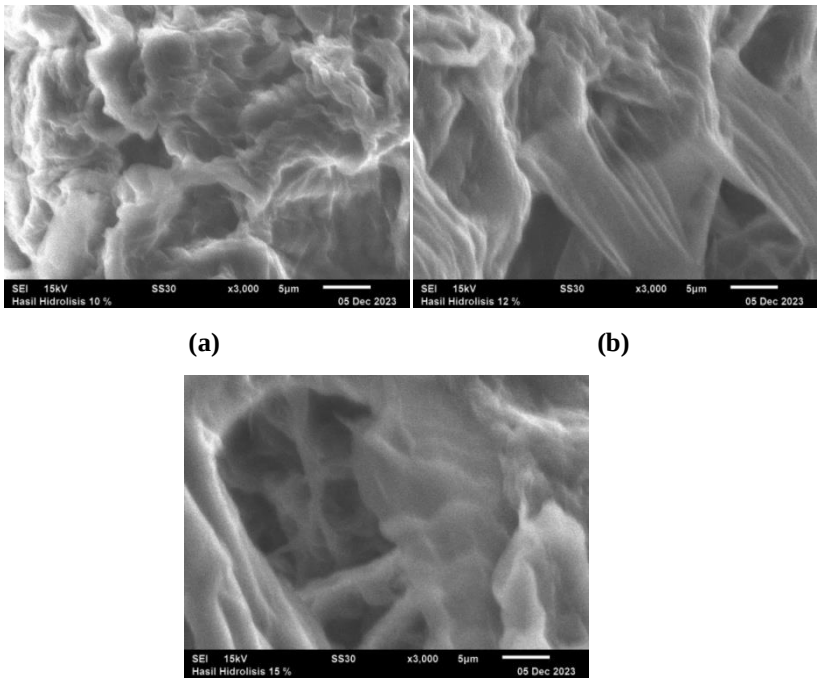

Figure 9. Typical scanning electron micrographs (a) CNF of 10% HCl, scale 5µm 3000x, (b) CNF of 12% HCl scale 5µm 3000x, (c) CNF of 15% HCl scale5µm 3000x

Figure 8 reveals that the hydrolysis products of cellulose at concentrations of 10%, 12%, and 15% exhibit irregular and porous structures. This structure arises from the hydrolysis process, which breaks down long cellulose chains into smaller glucose molecules. The pore structure observed in the SEM images indicates suitability for biomedical applications by providing space for cells and tissues to grow and develop. This is crucial for applications such as tissue regeneration and tissue engineering. The pores allow cells to migrate, adhere, and interact with each other, which are essential steps in the regeneration and engineering of tissues.

Furthermore, the pores in the SEM results also enhance cell-cell interactions. This is essential for optimal tissue function. Good cell-cell interactions enable communication and signaling between cells, which are critical for coordinating and regulating tissue function. The pores in the SEM results facilitate the diffusion of nutrients and oxygen into the tissue. This is vital for maintaining tissue health and viability. Nutrients and oxygen are indispensable for cellular metabolism and survival.

The pore structure in the SEM results can improve the biocompatibility of the material with the body. This is because the pores allow body tissues to grow into the material, helping to reduce the risk of implant rejection. However, among the HCl concentrations tested, the most suitable for biomedical applications is HCl with a concentration of 15%.

Hydrolyzed nanocellulose with 15% HCl concentration exhibits several advantages that make it potentially suitable for medical applications. Its enhanced porosity and active surface area enable better drug diffusion, interaction with biological molecules, and higher biocompatibility. Its improved mechanical properties make it stronger and more durable for medical implants and orthopedic devices. Additionally, its compatibility with biopolymers makes it ideal for fabricating tissue scaffolds and biodegradable drug delivery systems.

CONCLUSION

Delignification of cellulose using 2% NaOH at a temperature of 90° for 2 hours was successfully carried out where the cellulose obtained showed a white color and the XRD pattern showed crystals in accordance with the characteristics of cellulose. Hydrolysis of cellulose using HCl (10; 12; 15) % is able to break the amorphous chains of cellulose and produce CNF which is smaller in size. This is shown in the SEM analysis results which show small particle dimensions and an XRD pattern with high crystallinity (80.66; 79.06; 77.69)% with a small crystal size. The chemical structure shown by FT-IR has shown good cellulose crystals where the lignin and hemicellulose regions have been completely removed as indicated by the absence of C-O-C and carbonyl functional groups originating from lignin.

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