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Characterization of Nanocellulose from Orange Peel Waste

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ABSTRACT

Orange peel is a commercially available natural fiber with an increasing interest in using it as a raw material in a variety of applications due to its high cellulose concentration in the plant. This research aims to determine the preparation of nanocellulose from orange peel waste (OPW) by using chemical treatment of acid hydrolysis method. In order to provide the optimum conditions of nanocellulose of OPW which are possessed high crystallinity in their crystal structure by using acid hydrolysis method and the effects of various acid concentrations on the crystallinity index, crystallite size and morphology of cellulose nanocrystals were studied. However, based on the previous study, using OPW there is limited study has been reported on type of acid and optimum acid concentration as a parameter of using hydrolysis method. Therefore, in this study, the process of preparation OPW nanocellulose by using acid hydrolysis method with the best type of acid used of sulphuric acid (H_2SO_4) and hydrochloric acid (HCl), optimum acid concentration (30-40 wt%), constant hydrolysis time (120 min) and constant temperature (45 °C) is comprehensively studied. Based on the achieved outcomes, the H_2SO_4 emerges as the most favorable approach for acid hydrolysis technique, effectively yielding finely dispersed crystalline cellulose while mitigating undesirable aggregation effects. The optimal acid concentration of 30 wt%, coupled with a 120 minute hydrolysis duration and a temperature of 45 °C, yields the most favorable results in terms of both crystallinity index and crystallite size, reaching remarkable values of 87.69 % and 3.19 nm, respectively. The nanocellulose derived from OPW holds significant potential as an environmentally sustainable material, aligning harmoniously with prevailing global trends in design and development for enhanced sustainability.

1. Introduction

Citrus fruits, which include oranges, limes, grapefruits, and lemon, are among the most popular and well-known types of fruits worldwide. Due to its waste material, orange peel is one of the underutilised waste materials. Citrus fruits boast abundant vitamin C, a vital nutrient renowned for enhancing the immune system and promoting youthful skin appearance. Additionally, they

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encompass vitamin A and B, dietary fibers, folic acid, amino acids, as well as essential minerals including calcium, potassium, and phosphorus, all of which contribute positively to overall health [1-4].

The composition of all plant materials, including citrus fruits and natural lignocellulosic substances, comprises three essential organic constituents: cellulose, hemicelluloses, and lignin. Cellulose, comprised of linear D-glucose units, assembles into microfibrils that contribute to the polymer's robustness and resilience. On the other hand, hemicellulose, a type of polysaccharide, displays variable structures contingent upon the origin, including the plant type and tissue. Lignin, a complex amorphous polymer of substantial molecular weight, forms a three-dimensional network interlinked by phenylpropane monomers. Lignin plays crucial roles in offering structural support to the plant cell wall, conferring resistance against microbial agents, and contributing to the hydrophobic nature of the cell wall [5-8].

Alkaline treatment can be used to extract nanocellulose, a natural fibre, from cellulose that contains cementing materials such as lignin and hemicellulose. The alkaline treatment is critical for the production of highly pure cellulose nanocrystals [9-12]. Alkaline treatment increases the density of fiber by removing the nanocellulosic component that is hemicellulose and lignin by using sodium hydroxide (NaOH). This treatment remove lignin and hemicellulose and it also increase the amount of cellulose exposed on the fiber surface. Consequently, alkaline treatment increases the degree of crystallinity [13-16].

While acid hydrolysis with concentrated mineral acids stands as the most commonly employed technique for nanocellulose preparation, it bears significant shortcomings. These include environmental and human health hazards, equipment corrosion, excessive degradation of raw cellulose material, and high costs associated with the process. Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) have emerged as viable alternatives due to their moderate acidity levels. These acids effectively address the challenges tied to cellulose hydrolysis. By utilizing them, it becomes possible to efficiently produce nanocellulose from natural fibers, yielding nanoscale structures with high efficiency and impressive yields [17-19].

The hydrolysis process conditions, such as type of acid, acid concentration, constant hydrolysis temperature, and constant hydrolysis time are critical in the production of cellulose nanocrystals. As a result, the motivation of this project is to investigates the type of acid used, as well as the optimum acid concentration used during the acid hydrolysis treatment, as a parameter in order to develop nanocellulose from orange peel waste (OPW). The temperature and time will be considered a constant parameter and two different acidic is used during acid hydrolysis as a parameter which are sulphuric acid (H_2SO_4) and hydrochloric acid (HCl). As a result, the purpose of this research is to develop a strategy for the preparation and characterization of nanocellulose from OPW via chemical treatment methods such as acid hydrolysis. Due to the limitations of the previous study, only a few studies have been published on the effect of different type of acid and acid concentration as a parameter of acid hydrolysis of OPW nanocellulose. Additionally, the OPW nanocellulose will be analysed using X-ray Diffraction (XRD) analysis, Fourier Transform Infrared (FTIR) analysis and Scanning Electron Microscope (SEM).

2. Methodology

2.1 Raw Materials and Preparation

The raw material used in this experiment are orange peel waste (OPW). Approximately 30 g of the inner section of the mesocarp, which is albedo of OPW, was peeled and cleaned by washing it in water to remove dirt, dust, and other contaminants. In this study, albedo was chosen because it

contains low lignin therefore possibility to produce high yield and high crystallinity cellulose. For albedo and flavedo extraction, during maceration process, OPW was soaked in 50 ml of distilled water to soften the surface that is flavedo and albedo for an hour. Theoretically, soaking is intended to remove the flavedo that had accumulated on the surface of the albedo, and to soft shape that help for the sample to peel easily. Soaking is mainly used during the maceration process to remove germination inhibitors on the fiber such as, sand, dust and root that attached on the surface of fiber. maceration process can minimized the impurities that attached on OPW. By minimized the dirt that may impede during maceration process.

For 48 hours, the cutting OPW was dried in a drying oven machine set to 50 °C. The dried OPW was then powdered using an mortar and pestle, resulting in the powdered form. This process is repeated until the OPW powder is formed. The powdered were then stored in a Schott bottle to prevent air moisture before further treatment and analysis.

About 30 g of OPW powder will treated by using a 5 % of sodium hydroxide (NaOH) heated with 80 °C and will stirred for 3 hours. After that, the mixture was filtered and washed with distilled water for several time to remove lignin and hemicellulose that dissolve in the solution. Then, the resultant fiber was dried before used for further acid hydrolysis.

The acid hydrolysis procedure was carried out using distinct concentrations of sulfuric acid (H_2SO_4) and hydrochloric acid (HCl). Various parameters were involved in this hydrolysis, including the type of acid and its concentration, along with a consistent hydrolysis time and a fixed temperature. The acid concentration parameter, ranging from 30 to 40 wt.%, was selected. The hydrolysis process involved subjecting the cellulose from OPW to these defined parameters. Approximately 30 g of OPW was combined with H_2SO_4 and HCl, respectively. The resulting mixture was continuously stirred using a magnetic stirrer until the designated hydrolysis time was reached. Subsequently, the cellulose was dialyzed multiple times with distilled water until achieving a stable pH. Following this, the samples were dried in an oven at 40 °C for three days. The resulting OPW nanocellulose were preserved at room temperature, awaiting further analysis.

2.2 X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis will be conducted on OPW to assess the cellulose crystallinity. For this study, the nanocellulose's crystallinity from OPW was examined using a PAN analytical X'PERT PRO MPD X-ray diffraction apparatus, operating at 40 kV and 30 mA. The diffraction profile was obtained with a temperature increase of 2 °C per minute. The samples were subjected to step-scan mode, ranging from a 2 angle of 5 to 70, utilizing a monochromatic Cu-Kα radiation source (λ = 1.5406 Å). The Segal method was employed to determine the crystallinity index, Crl, as outlined in Eq. 1. Here, I_{002} represents the maximum peak intensity at approximately 2θ = 22° to 24° for crystalline cellulose, and I_{am} denotes the peak intensity of the amorphous region's diffraction at about 2θ = 15° for cellulose.

$$\text{Crl (\%)} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

The determination of crystallite size involves the utilization of the Scherer equation outlined in Eq. 2. In this equation, the variable K represents a shape factor, with K being the Scherrer constant that is most precisely tailored to the specific nanocrystal shape. The variable λ signifies the wavelength (1.5418 Å), while β corresponds to the full width at half maximum intensity (FWHM). Additionally, θ stands for half of the Bragg angle at the peak's maximum, expressed in radians.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

2.3 Fourier Transform Infrared (FTIR) Analysis

Fourier Transform Infrared (FTIR) spectroscopy will be used to study the elemental chemical composition of different chemical stages. This analysis was also used to support the result of the XRD analysis in order to show whether the hemicellulose, lignin, and other impurities had been removed during the alkaline treatment by investigating their functional groups. The elemental chemical composition of OPW nanocellulose powders was analysed by using an FT-IR-6100 Spectrum GX-FT-IR spectrophotometer (Perkin Elmer, Germany) machine as and carried out at room temperature. FTIR spectral analysis was performed within the wave number range of 400-4000 cm^{-1}.

2.4 Scanning Electron Microscopy (SEM) Analysis

Scanning Electron Microscop (SEM) analysis gives excellent imaging that is important in studying the shape of microscopic structures by scanning the ruptured surface of materials. The SEM is being used to examine this analysis. SEM was employed in this study to analyse the surface morphology of OPW after introduced to the acid hydrolysis method. Before the study, a small sample was coated with gold using a little sputter coater because the material utilised is fibre which is hygroscopic, and requires coating to avoid charge. Images of the samples were captured using an acceleration voltage of 2 kV, a resolution of around 10 nm, and magnifications ranging from 5 to 1,000,000X.

3. Results

3.1 X-Ray Diffraction Analysis (XRD)

After orange peel waste (OPW) nanocellulose undergoing the acid hydrolysis treatment with sulphuric acid (H_2SO_4) and hydrocloric acid (HCl), the X-Ray Diffraction (XRD) patterns were analyzed in order to study the effect of the parameters that were used. Based on Figure 1, it was determined that a comparison of two samples by different types of acids for acid hydrolysis that is H_2SO_4 and HCl with concentration of 30-40 wt% and constant time (120 min) and fixed temperature (45 °C). Analysis of the XRD graph reveals a notable increase in crystallinity peaks after undergoing alkaline treatment and acid hydrolysis. This observation is supported by the diffraction pattern, where the presence of a broad peak at approximately 15˚ suggests the presence of an amorphous structure. Consequently, it can be deduced that both acids have resulted in a cellulose type I structure. The results indicate that nanocellulose exhibits three distinct diffraction peaks, specifically at 2θ values of 15°, 22°, and 35° [20, 21].

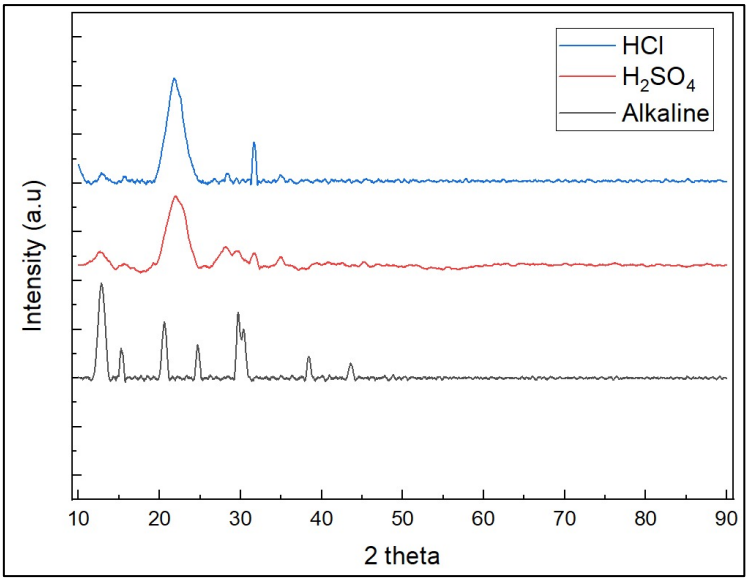

Fig. 1. XRD analysis of OPW nanocellulose after introduced to alkaline treatment and acid hydrolysis method

The crsytallinity index for isolated nanocellulose from OPW can be seen on Table 1. H_2SO_4 had crsytallinity index 87.69 %, while HCl is 78.00 %. This difference due to the type of acid used and due to the strong acid HCl it will result lower on crystallinity index indicates the amorphous and crystalline region could be highly significantly degraded. This suggests that the introduction of a strong acid not only disrupts the amorphous portion of cellulose but also impairs its crystalline structure. As the crystallinity index rises, there is a concurrent increase in crystallite size. This phenomenon is attributed to the expansion of the crystallite surface area, which corresponds to the reduction in amorphous cellulose regions [22, 23].

Utilizing H_2SO_4 in acid hydrolysis facilitates the breakdown of the cellulose's amorphous region, leading to the production of nanocellulose characterized by a notably high crystallinity index. However, the application of a more potent acid like HCl can result in the impairment of the crystalline segment during the acid hydrolysis procedure, consequently causing a reduction in the crystallinity index. Consequently, the use of the stronger acid HCl, particularly at a higher concentration of 40 wt%, can induce the cellulose fibers to undergo charring throughout the acid hydrolysis process. This outcome ultimately manifests as a transformation of OPW pulp into a blackened state, followed by dissolution within the acidic medium. These circumstances collectively hinder the feasibility of conducting accurate characterizations for analysis purposes.

Table 1
Cellulose intensity peak and the respective CrI

Sample	2θ (Amorphous)		2θ (Crystalline)		Crystallinity Index %
	Degree	Intensity (I_{am})	Degree	Intensity (I_{002})	
Untreated OPW	15.82	1153	21.67	1508	23.54
Alkaline Treated OPW	15.68	853	22.73	4294	80.14
30wt% (H_2SO_4)	12.75	993	22.94	8064	87.69
40wt% (H_2SO_4)	-				
30wt% (HCl)	12.99	321	21.99	1459	78.00
40wt% (HCl)	-				

Furthermore, in terms of crystallite size from Table 2, it is evident that H_2SO_4 yields a smaller crystallite size compared to HCl, primarily attributed to the pronounced erosion of granule surfaces.

In line with findings by Wulandari *et al.,* (2016) and Bacha (2022) [24, 25], nanocellulose derived from acid hydrolysis typically exhibits diminished particle dimensions. This substantiates the rationale behind opting for the acid hydrolysis method to obtain nanocellulose. Consequently, it can be inferred that subtle alterations in both crystallinity index and crystallite size directly correlate with acid strength, as the hydrolysis time remains constant. However, with the fact that high acid concentrations, particularly at 40 wt%, as elucidated by H_2SO_4 and HCl, are adept at disrupting hydrogen bonds. This disruption facilitates penetration into both amorphous and crystalline cellulose regions, ultimately causing sample combustion and dissolution within the solution. Similar observations are also observed in the investigations conducted by Yu *et al.,* (2021) and Bolat *et al.,* (2023) [26, 27].

Table 2
Crystallite size of nanocellulose OPW at different parameter

Sample	Position (°2Th.)	FHWM (°2Th.)	Crystallite Size (nm)
30 wt% (H_2SO_4)	21.8879	2.6765	3.19
40 wt% (H_2SO_4)	-		
30 wt% (HCl)	22.2901	1.6059	5.34
40 wt% (HCl)	-		

3.2 Fourier Transform Infrared Spectroscopy Analysis

Figure 2 displays the Fourier Transform Infrared (FTIR) spectra of OPW nanocellulose and pretreated OPW pulp following alkaline treatment. In this figure, it's evident that the OPW nanocellulose spectrum closely resembles that of the pretreated OPW pulp, particularly concerning the characteristic cellulose peaks. A more precise measure of crystallinity is the ratio of absorbance at 1372 cm^{-1} (C-H bending) to 2900 cm^{-1} (C-H stretching). The peaks at 1644 and 897 cm^{-1} correspond to the H-O-H stretching vibration of absorbed water in carbohydrates and the C_1-H deformation vibrations of cellulose, respectively. The acid hydrolysis process efficiently removed amorphous cellulose from the surface, exposing more C-OH, C-O-C, and C-C bonds, leading to an increased stretching absorbance. In the FTIR spectrum of OPW nanocellulose, the broadening of the OH absorption band from 3342 cm^{-1} to 3409 cm^{-1} was observed. This shift is not solely due to sulfuric acid hydrolysis but also attributed to water adsorption. Furthermore, the broadening of the absorption band at 3342 cm^{-1} can be attributed to the presence of the amorphous fraction of cellulose [28-31].

Hence, the FTIR spectrum comparison between OPW nanocellulose after H_2SO_4 and HCl hydrolysis suggests the successful isolation of nanocellulose from OPW pulp through the acid hydrolysis approach. Consequently, it can be deduced that the OPW nanocellulose synthesized in this study is nearly pure, primarily containing minute quantities of lignin and other non-cellulosic constituents.

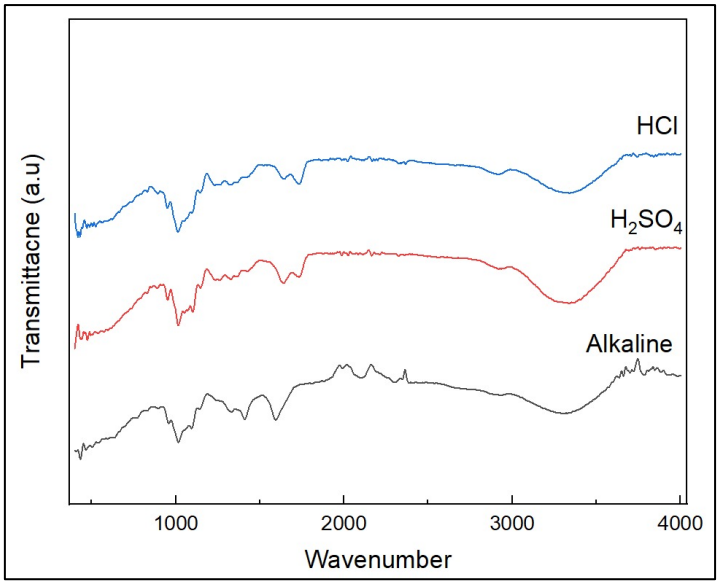

Fig. 2. FTIR spectra of OPW nanocellulose after introduced to alkaline treatment and acid hydrolysis method

3.3 Scanning Electron Microscopy (SEM) Analysis

After alkaline treatment undergoes to acid hydrolysis by being immersed in a H_2SO_4 and HCl solution with a 30-40 wt% concentration. The fibers were subsequently filtered and thoroughly rinsed with distilled water until reaching a neutral pH level. Following this, the fibers were dried in an oven at 40 °C for a duration of 24 hours. As depicted in Figure 3, there are modest variations in the fiber's colour on H_2SO_4 result the white colour of OPW nanocellulose powder. While HCl result the dark grey colour of OPW nanocellulose powder. The sample continues to undergo SEM analysis in order to assess the surface morphology of acid hydrolysis.

Fig. 3. Image of acid hydrolysis of OPW (a) H_2SO_4 and (b) HCl

Figure 4 showed the morphology surface are rod-like shape with might be due to degradation primarily occurs in the amorphous cellulose. H_2SO_4 recognized most widely used for acid hydrolysis because process is simple and result with highly crystalline, stiff and effective on elimination of amorphous. Figure 5 illustrates the surface morphology under these conditions with HCl, revealing the absence of cellulose fibers and the presence of significant aggregation. Compared to H_2SO_4, HCl

has a higher corrosion resistance, and its nanocellulose fibres are well-defined and primarily aggregate on a large scale. Due to the strong acid of HCl, it make the OPW cellulose dissolves with the acid. It is suggested that H_2SO_4 is the optimal choice for acid hydrolysis, as it is capable of generating finely dispersed crystalline cellulose with minimal aggregation, as demonstrated by Huntley *et al.,* in 2015 [32].

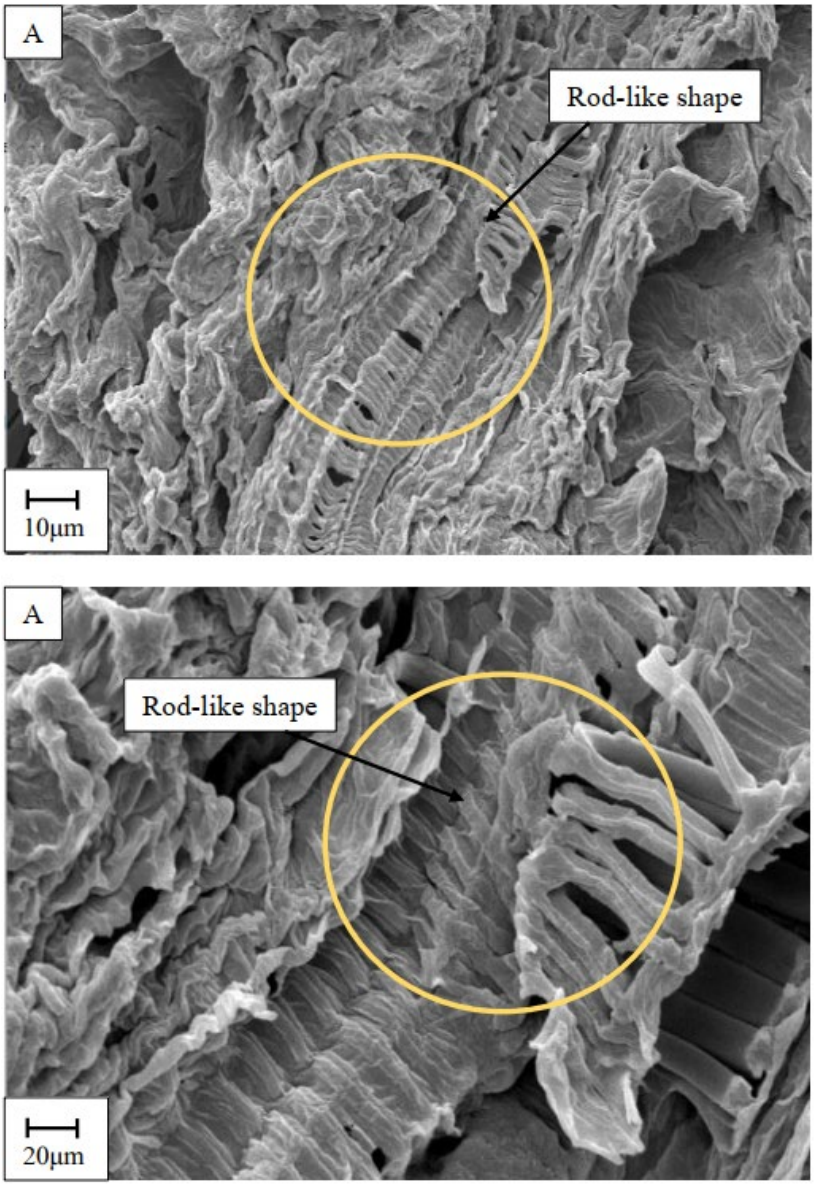

Fig. 4. Surface morphology for H_2SO_4 on scale 10µm and 20µm

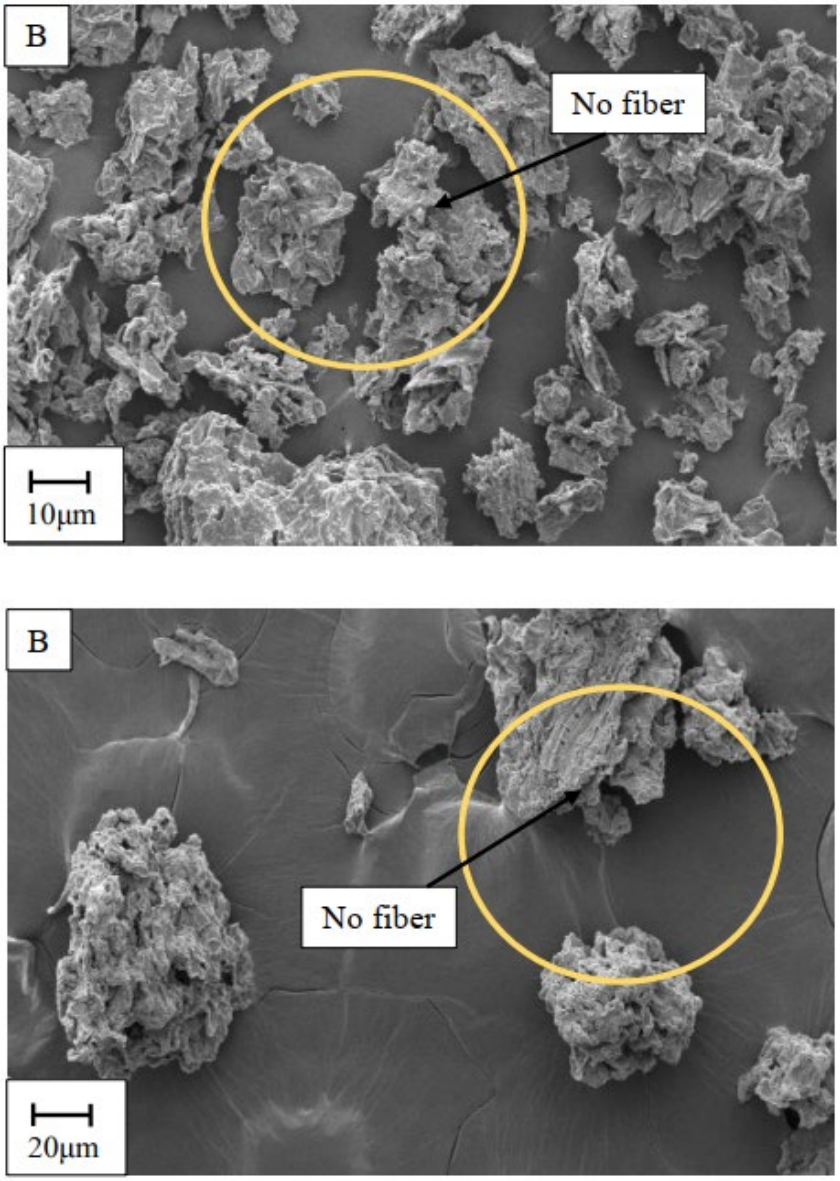

Fig. 5. Surface morphology for HCl on scale 10µm and 20µm

4. Conclusions

In conclusion, the successful preparation of nanocellulose from orange peel waste (OPW) was achieved by adhering to specific parameters, involving acid type, concentration, temperature, and time. The optimal conditions entailed a 30 wt% concentration of sulphuric acid (H_2SO_4) for nanocellulose isolation, along with a constant 120 minutes hydrolysis time and 45 °C temperature. This nanocellulose was obtained through a two-stage process involving an initial alkaline treatment with 5 wt% sodium hydroxide (NaOH) followed by acid hydrolysis using either sulphuric acid (H_2SO_4) or hydrochloric acid (HCl). The following research objective centered on assessing OPW nanocellulose crystallinity and crystallite size through X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) Spectroscopy, revealing optimal conditions for heightened crystallinity and size. The final objective aimed to study the nanocellulose OPW morphology via Scanning Electron Microscopy (SEM), confirming successful impurity removal through alkaline treatment and acid hydrolysis method.

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