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Microcrystalline Cellulose Production from Pineapple Leaves and Crowns using Trifluoroacetic Acid

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Pineapple leaves and crowns (PLC) have high cellulose contents of 74.50% and 51.20%, respectively, positioning them as promising sources to produce microcrystalline cellulose (MCC). This study examines the effect of hydrolysis time and acid concentration on MCC yield and crystallinity. Trifluoroacetic acid (TFA) was utilised in the acid hydrolysis process, applied at concentrations of 40% (v/v) and 65% (v/v) at 45 min and 90 min, respectively. The produced MCC is distinguished by its morphology, yield, crystallinity index, and functional groups. The highest yield of dried MCC produced from 2 g of PLC was 16.25% at a process condition of 40% (v/v) for 90 min, whereas the highest crystallinity index was obtained at 67.79% for hydrolysis at 65% (v/v) of TFA at 90 min. An irregular rod-like structure and inconsistent diameter of the obtained MCC showcases notable physical properties. This study expected the presence of carbonyl groups on the surface of MCC; however, due to insufficient energy for esterification at low temperatures, the carbonyl group was absent on the surface of MCC samples, as indicated in the FTIR spectra. This study offers a potential technique for investigating the use of TFA as a sole material in both pre-treatment and hydrolysis steps, which could simplify the extraction process.

Keywords: Microcrystalline cellulose; acid hydrolysis; trifluoroacetic acid

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Vast agricultural waste has led to severe environmental repercussions due to waste management limitations. Agricultural waste, comprising cellulose, hemicellulose, and lignin, presents an opportunity for conversion into value-added products, particularly cellulose [1-3]. Cellulose, formed by D-glucopyranose molecules joined by β, 1-4 glycosidic linkages, possesses 3-hydroxyl groups on its monomer, known as anhydroglucose units (AGU) [4-5]. Cellulose has been extensively studied for its products and derivatives to be used in various applications because cellulose is an inexhaustible natural polymer characterised by being biodegradable, biocompatible, non-toxic, and having high mechanical strength. These properties are highly favoured by researchers and industries alike [6-7]. Pineapple leaves and crowns exhibit significant cellulose content, which is 74.50% and 51.20%, respectively, followed by hemicellulose, lignin, and ash [8-10]. Considering their high content of cellulose, pineapple leaves and crowns emerge as prime candidates for extracting microcrystalline cellulose (MCC).

Microcrystalline cellulose (MCC), a white and odourless cellulose product, can be synthesised through various means, including acid hydrolysis, enzyme hydrolysis, and steam explosion, but the most conventional method used is partial acid hydrolysis [11]. MCC usually exhibits a particle size diameter of 50 μm and a length of 100–1,000 μm, rendering it with exceptional characteristics such as high surface area, biodegradability, biocompatibility, and non-toxicity, qualities highly sought after across various fields [12]. Other than that, a high crystallinity ranging from 55% to 80% is also one of the main attributes of MCC [13]. Very few studies on the extraction of microcrystalline cellulose from pineapple leaves and crowns have been reported. A study reported by [14] characterised the isolated microcrystalline cellulose from pineapple leaves using hydrochloric acid (HCl) for its organoleptic test, water solubility test, pH test, starch test, and loss of drying test. Other than that, [15] extracted microcrystalline cellulose from pineapple leaf fibres modified with aminosilanes for hydrogen sulphide (H_2S) removal, while [16] produced MCC from pineapple leaves as well to convert it into hydrocar as a carbon source to detect mercury ions (Hg^{2+}).

Acid hydrolysis stands as the most frequently used method to obtain MCC, with many researchers favouring strong acids such as sulphuric acid, hydrochloric acid, phosphoric acid, hydrobromic acid, and nitric acid [17]. In this process, the hydrogen ion of

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the acid attacks the glycosidic bond of the microfibrils, resulting in the hydrolysation of the amorphous region while leaving the crystalline region intact [18]. Sulphuric acid is preferred for degrading cellulose due to its excellent hydrolysis efficiency and good dispersibility. However, its strong acidity can degrade the cellulose excessively, and the presence of sulphate groups can influence its thermal stability [19]. Although other acids such as hydrochloric acid, oxalic acid, and maleic acid have been investigated for cellulose degradation, they are generally considered inferior to sulphuric acid. Trifluoroacetic acid (TFA), a monocarboxylic acid, is one of the strong acids with a pK_a of 0.23 in water at ambient temperature. It has a low boiling point of 71.8 °C and is miscible with most organic solvents as well as water [20]. Moreover, its high volatility enables easy removal and recovery through evaporation [21], thereby streamlining the product recovery process. TFA is able to degrade hemicellulose and lignin, offering an alternative to alkali and bleaching treatments, thus reducing the need for additional chemicals. This was reported in a study by [22] that demonstrated TFA's potential to hydrolyse cellulose and hemicellulose from Loblolly pine. Other than that, TFA has also been used by [23] to pre-treat cereal straws to produce bioethanol or cellulosic products. The feasibility of using TFA to pre-treat the straw is supported by successfully culturing *Pichia pastoris* GS115 on M9 mineral plates with the TFA reaction supernatant. Additionally, this study determines TFA's potential to degrade cellulose, xylan, and lignin from various lignocellulosic materials such as wheat straw, rice straw, corn stover, and sabai grass.

This work extracted MCC from pineapple leaves and crowns (PLC) under different TFA concentrations and reaction time conditions. The key characteristics investigated include surface morphology, diameter size, functional groups, and crystallinity index. The primary objective was to investigate the potential of agricultural biomass as a low-cost source of MCC and assess the viability of using TFA to hydrolyse the cellulosic chains, thereby producing a carbonylated surface of MCC. Given the emerging significance of organic carbonyl polymers as alternatives to inorganic electrode materials in lithium and sodium ion batteries [24]–[26], this study lays the groundwork for further research on TFA's role in carbonyl polymer production.

EXPERIMENTAL

Chemicals and Materials

Pineapple leaves and crowns (PLC) were gathered from a local pineapple plantation in Selangor. In this investigation, the following chemicals were utilised: trifluoroacetic acid (TFA, Sigma Aldrich; ReagentPlus®, 99%, USA), anhydrous sodium hydroxide pellets (NaOH, 98%, R&M Chemicals, Malaysia), and 30% (w/w) hydrogen peroxide (H_2O_2, Sigma Aldrich, USA).

Raw Materials Preparation

Pineapple leaves and crowns (PLC) were thoroughly washed and cut into smaller pieces. Then, samples were dried in the oven at 60 °C for 24 hours. Following drying, the dried leaves and crowns were ground into powder and stored in separate containers in a dry place.

Alkali Treatment

At 90 °C for one hour, 2.0 g of PLC (weight ratio 1:1) was mixed with 40 ml of 5% (w/v) NaOH with continuous stirring. The solution was cooled to ambient temperature and vacuum-filtered to sediment solid PLC on the filter paper. Multiple washings with deionised water were conducted until the pH reached 7. The alkali-treated PLC was then dried at 60 °C for 24 hours [2].

Bleaching

The dried alkali-treated PLC was mixed with 40 ml of 5% NaOH and 16% H_2O_2 (ratio 1:1) at 55 °C for 2 hours under continuous stirring [2]. Afterward, it was cooled to room temperature and filtered using vacuum filtration. The bleached PLC was washed with deionised water several times and then dried in the oven at 60 °C for 24 hours.

Isolation of MCC

Bleached PLC (1g) was hydrolysed with 20 ml of different acid concentrations using TFA (i.e., 40 and 65% (v/v)) and reaction times (i.e., 45 and 90 min) at 30 °C, as shown in Table 1. Quenching was conducted to stop the reaction, and excess acid was removed by successive washing and centrifugations at 5,000 rpm for 20 minutes. The sediment was then dialysed against deionised water until a neutral pH was achieved. The resulting MCC was dried in an oven at 60 °C for 24 hours.

Table 1. Hydrolysis process conditions of MCC extraction from PLC.

Samples	TFA concentration (% (v/v))	Time (min)	Temperature (°C)
PLC-1	40	45	30
PLC-2	40	90	
PLC-3	65	45	
PLC-4	65	90	

Morphological Analysis using Field Emission Scanning Electron Microscopy (FE-SEM) and Fourier Transform Infrared (FTIR) Spectroscopy

The surface morphology of the MCC samples was examined using field emission scanning electron microscopy (FE-SEM, Hitachi SU8020, Japan). The samples were gold-coated and were characterised under magnifications ranging from 100x to 1,000x. The diameter of the MCC was determined using ImageJ software, with 100 fibres selected from the images. The functional groups of the samples were characterised at room temperature using Fourier transform infrared spectroscopy (FTIR; Spectrum One, Perkin Elmer, USA) within the range of 4,000-450 cm^{-1}, with 4 cm^{-1}, and 32 resolutions and scans, respectively.

X-ray Diffraction (XRD)

Dried MCC samples were characterised for their crystallinity using an X-ray diffraction (Rigaku Smartlab, Japan) machine using Cuk_{α} radiation at a generator voltage of 45kV, a current of 4mA, and a scanning speed of 2 s^{-1} at $2\theta = 5^{\circ}$ to 40° at room temperature. The crystallinity index (CrI) of the samples was calculated using Segal's equation:

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

Where I_{002} is the maximum intensity of the diffraction at (002) peak for native cellulose at 2θ between 22° and 23° and I_{am} is the minimum intensity related to the amorphous scattering at 2θ between 18° and 19° [11].

RESULTS AND DISCUSSION

Extraction of Microcrystalline Cellulose

The TFA concentrations and reaction times were selected based on the acid hydrolysis process of cellulose using sulphuric acid since most studies used those ranges to extract crystalline cellulose [16], [27]–[31]. The extent of TFA in hydrolysing cellulose can be compared to sulphuric acid when choosing sulphuric acid process parameters as a reference. Table 2 lists the yield of MCC for each sample. PLC-2 recorded the highest yield at 16.25%, achieved with a TFA concentration of 40% (v/v) and a reaction time of 90 min. For PLC-3, with a TFA concentration of 65% (v/v) and a reaction time of 45 min, the MCC produced was 13.49%. PLC-4 produced the lowest yield at 7.10%, which might be attributed to the dissolution of cellulose due to the highest TFA concentration and the longest reaction time. According to [23], TFA may dissolve but may not degrade the cellulose during the pre-treatment of the wheat straw at 60 °C for 16 hours. However, the low yield of PLC-1 could be attributed to an inefficient hydrolysis process and purification and recovery procedures. A low acid concentration and shorter reaction time impeded both the extent and rate of cellulose depolymerisation. Additionally, losses incurred during washing and filtration steps reduced the total mass of recovered MCC, thereby diminishing the overall yield. The MCC yields obtained in this study are comparatively higher than those reported in [14], where 7.25% of MCC from pineapple leaves was produced using hydrochloric (HCl) acid. This finding suggests that lower concentrations of TFA require longer reaction times to obtain high yields of MCC, whereas higher concentrations enable higher yields within shorter reaction times.

Field Emission Scanning Electron Microscopy (FE-SEM)

Figure 1 depicts the morphological structure of samples for PLC-1, PLC-2, PLC-3, and PLC-4 and their diameter distributions. Microcrystalline cellulose usually exhibits a rough surface and an uneven rod-like structure. The formation of individual fibres is associated with the removal of non-cellulosic components such as lignin and hemicellulose during alkali and bleaching treatments, initially causing fibre aggregation [11], [32]. Acid hydrolysis subsequently causes defragmentation of the cellulose fibre arrangement, resulting in rod-shaped MCC with a rough surface [11]. The MCCs generated exhibit inconsistencies in diameter, as depicted in Figure 1. The mean diameters for PLC-1, PLC-2, PLC-3, and PLC-4 were 4.89±1.37, 4.80±1.62, 4.90±1.68, and 5.23±1.53 µm, respectively. The difference in mean diameters for PLC-1, PLC-2, and PLC-3 was not significant, while PLC-4 had the biggest mean diameters. Notably, from Figure 1 (a3 to d3), all samples demonstrated a relatively broad diameter distribution with different ranges.

Table 2. Yield of MCC extracted from PLC under different conditions of acid hydrolysis.

Samples	TFA concentration (% (v/v))	Time (min)	Temperature (°C)	Yield (%)
PLC-1	40	45	30	7.86
PLC-2	40	90		16.25
PLC-3	65	45		13.49
PLC-4	65	90		7.10

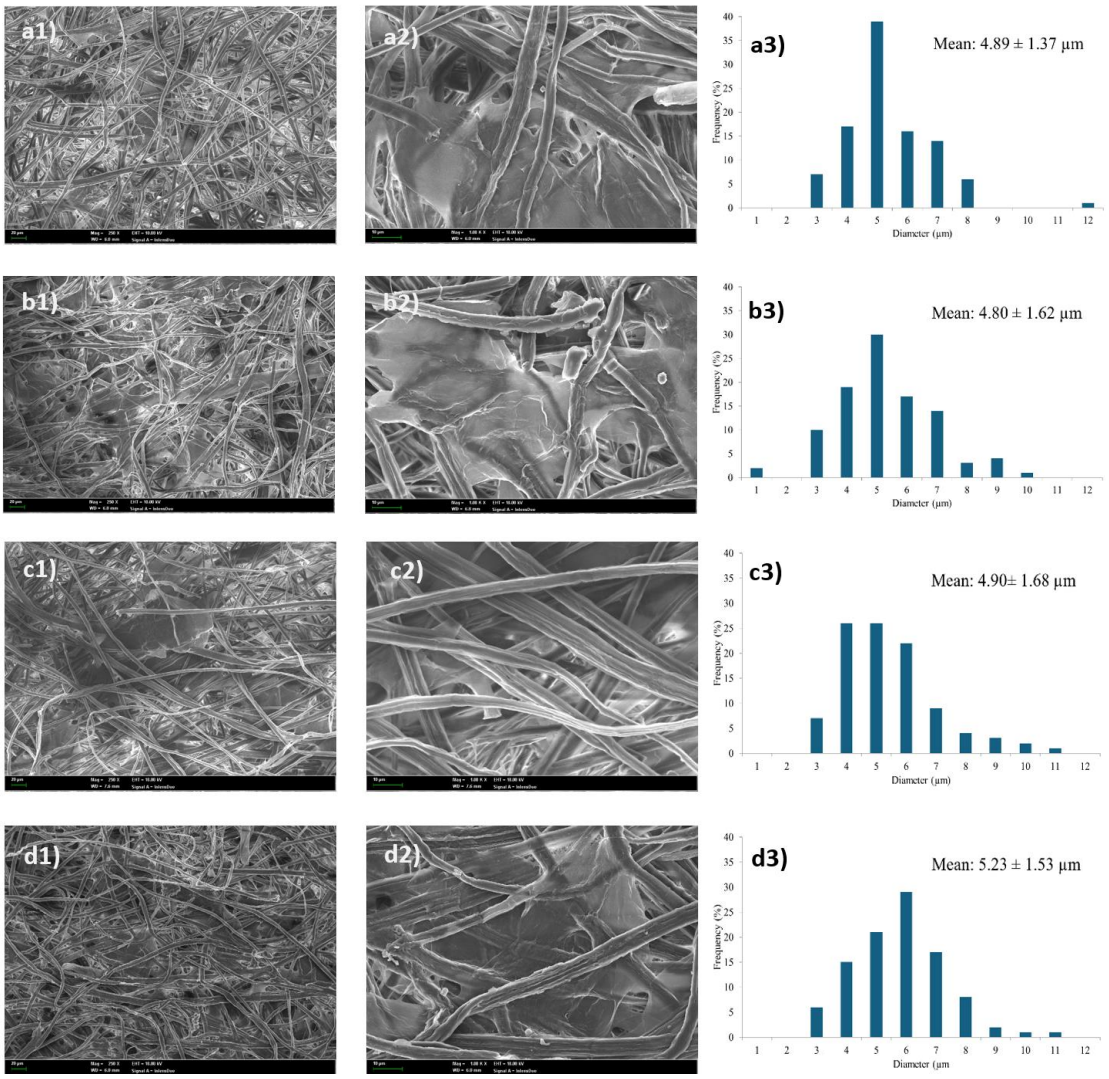

Figure 1. FE-SEM images at magnifications of 250x and 1,000x and diameter distribution of (a) PLC-1, (b) PLC-2, (c) PLC-3, and (d) PLC-4.

PLC-1 had diameters ranging from 3 µm to 12 µm, while PLC-2 ranged from 1 µm to 10 µm. PLC-3 and PLC-4, however, shared a similar diameter distribution, ranging from 3 µm to 11 µm. Conversely, despite the diameter discrepancies of the MCCs, it can be observed that the mode of the MCCs' diameters was centred around 4 µm to 6 µm. It is noteworthy that longer reaction times applied to the hydrolysis process appear to affect the surface morphology and diameter size of MCC, despite variations in TFA concentrations. Nevertheless, all samples exhibit individual fibres, indicating the absence of lignin and hemicellulose. Similar surface characterisation of MCC from jute [33] and kenaf fibre [32] has also been observed.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of the samples are shown in Figure 2, with vibrational assignments tabulated in Table 3. All MCC samples revealed nearly similar ranges of spectra, suggesting similar chemical compositions among the samples. Comparable spectra of MCC obtained from pineapple leaves were reported in previous studies [14], [34].

The band at 3,481-3,085 cm^{-1} is assigned to inter- and intra-molecular O–H stretching vibrations. The decreased absorbance intensity at this peak shows the breaking down of the hydrogen bond between the cellulose molecule chains during hydrolysis [35]. A low intensity around 2,875 cm^{-1} is associated with C–H band stretch, and it is caused by the appearance of -CH_2 moieties in MCC samples. Carbonyls of trifluoroacetyl esters are typically present at bands 1,790-1,690 cm^{-1} [36]. However, no peak was observed at this band, indicating that the carbonyl group is not deposited on the surface of MCC samples due to insufficient energy for esterification of the MCC surfaces with the carbonyls of trifluoroacetyls at low heating during hydrolysis. This is because it requires adequate heat and an acid catalyst to generate the required energy to remove the -OH from TFA [37].

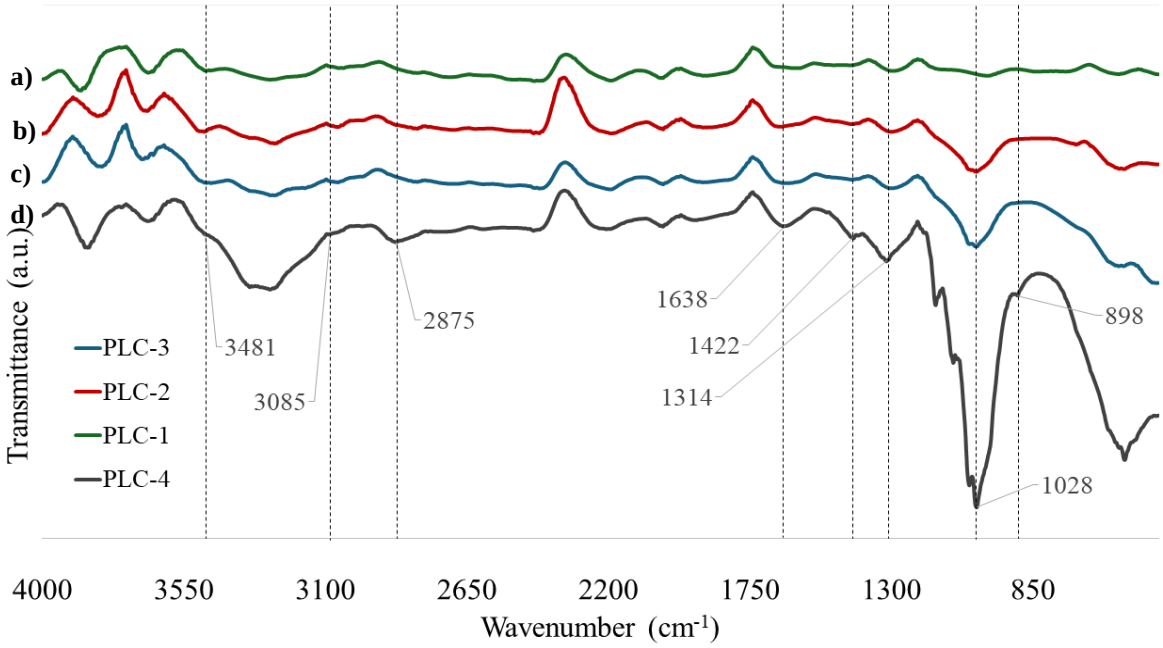

Figure 2. FTIR spectra of a) PLC-1, b) PLC-2, c) PLC-3, and d) PLC-4.

Table 3. Peak assignment of FTIR spectrum for PLC-1, PLC-2, PLC-3, and PLC-4.

Peak frequency (cm^{-1}) for PLC-1, PLC-2, PLC-3, and PLC-4	Peak assignment	References
3,481-3,085	O–H stretching	[35], [15], [38]
2,875	C–H band stretching	[29], [35]
1,638	Adsorbed water molecules	[35], [15]
1,422 and 1,314	-CH or CH_2	[29], [35], [38]
1,028	Ring stretching	[35]
900	Asymmetric out-of-plane ring stretching	[35], [38]

This peak could also correspond to small amounts of hemicellulose in the samples [35]. The bands at 1,422 and 1,314 cm^{-1} are attributed to -CH or CH_2 vibrations, which decrease their intensity and increase the degree of oxidation. Ring stretching is assigned at a range around 1,028 cm^{-1}, showing that the degradation of the pyranose ring in MCC samples is almost absent. The band at around 900 cm^{-1} is related to asymmetric-of-plane ring stretching in cellulose, ascribable to β-glycosidic linkage and the amorphous region in the samples. A decrease in the intensity of the peak means an increase in the crystallinity of the MCC [38].

X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) of all MCC samples is presented in Figure 3. XRD analysis is attributed to the crystalline region of native cellulose (Cellulose I), typically present at peaks 2θ of 15°, 16°, and 23° [39].

The diffractograms for PLC-1, PLC-2, and PLC-3 show peaks at 2θ of 16° and 23°, while PLC-4 peaks are depicted at 2θ of 16° and 22.7°. The crystallinity index of each sample is listed in Table 4.

A higher concentration of TFA and reaction time (i.e., 65% (v/v) and 90 min) applied to PLC-4 resulted in the highest crystallinity (i.e., 67.79%), while the lowest crystallinity was observed in PLC-1 (i.e., 57.72%), where the lowest acid concentration and shortest reaction time (i.e., 40% (v/v) and 45 min) were carried out. This observation indicates that both acid concentration and reaction time during the hydrolysis process significantly affect the crystallinity index of MCC samples. Increasing TFA concentration and prolonging the reaction time tend to enhance the crystallinity of MCC extracted from PLC. MCC with a high crystallinity

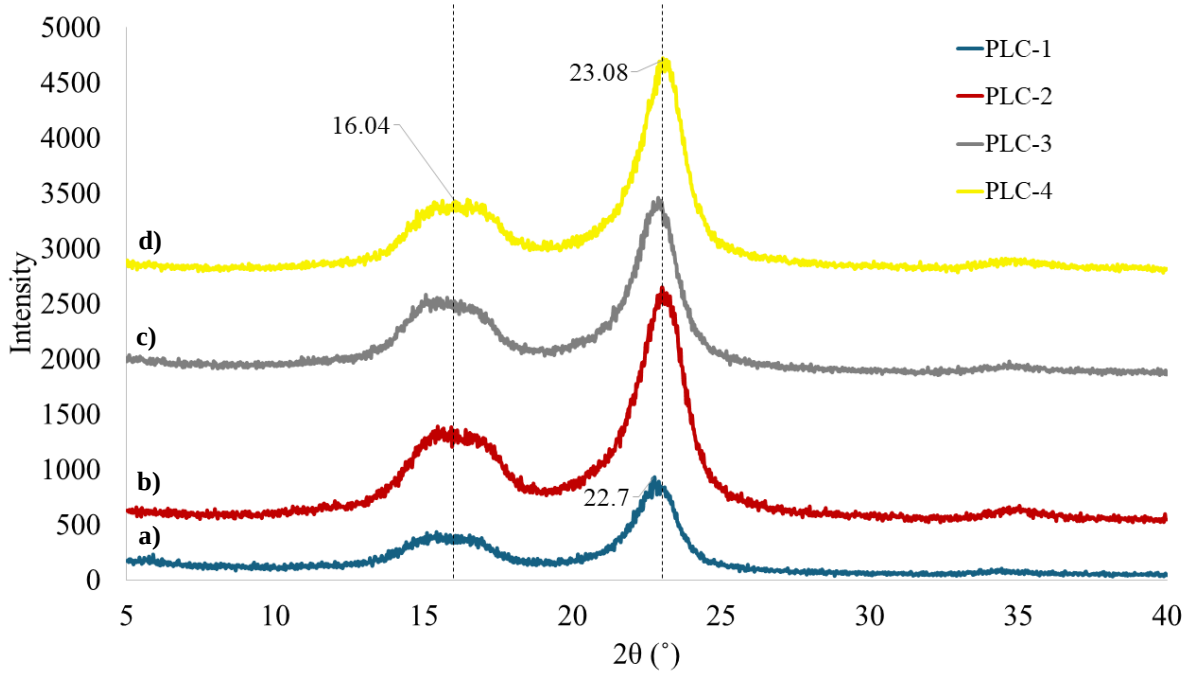

Figure 3. X-ray diffraction patterns of a) PLC-1, b) PLC-2, c) PLC-3, and d) PLC-4.

Table 4. Crystallinity index of PLC-1, PLC-2, PLC-3, and PLC-4.

Samples	Crystallinity index (%)
PLC-1	57.72
PLC-2	58.29
PLC-3	60.68
PLC-4	67.79

index of 79.21% was reported when pineapple leaf fibres were hydrolysed using 3.5 M HCl at 50 ˚C for 12 hours [15]. Another study reported a crystallinity index of 70% for MCC extracted from pineapple leaf fibres under processing conditions of 2 N HCl at 90 ˚C for 15 min [34].

CONCLUSION

In conclusion, MCC was successfully extracted from low-cost and abundant PLC waste using the hydrolysis of strong-acid TFA. Morphological analysis revealed a rod-like shape of micro-sized fibrils with a rough surface, while FTIR spectra confirmed the presence of cellulose chemical structure. However, the absence of the carbonyl group of trifluoroacetyl in the spectrum suggests that it does not exist on the surface of MCC. Additionally, a relatively high crystallinity index was obtained at higher acid concentrations and longer reaction times (i.e., 65% (v/v) and 90 min). This study holds potential for identifying specific strategies and patterns to produce a carbonylated surface of MCC, contributing to advancements in cellulose modifications. Moreover, the findings suggest the possibility of simplifying the MCC production method by incorporating TFA into pretreatment steps, potentially eliminating the need for dialysis and shortening the MCC recovery process, giving TFA's ease of evaporation. By optimising TFA utilisation and exploring its multifaceted applications, future research endeavours could further refine MCC extraction techniques and expand its potential applications across various industries.

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