EFFECTS OF ACID HYDROLYSIS ON THE EXTRACTION OF CELLULOSE NANOCRYSTALS (CNCs): A REVIEW

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The potential utilization of cellulose nanocrystals (CNCs) as reinforcing materials has lately attracted significant research attention. This is mainly due to their versatility and suitability for various applications in fields such as food packaging, cosmetics, biomaterials and pharmaceuticals. Several methods have been reported in the literature for isolating CNCs from plant sources, including acid hydrolysis, mechanical treatment and enzymatic hydrolysis, resulting in CNCs with different dimensions, crystallinities and thermal stabilities. However, acid hydrolysis using sulphuric acid (H_2SO_4) remains the favourite, as it requires shorter time and produces a stable suspension, with high crystallinity, compared to other methods. Sulphuric acid hydrolysis is generally performed with 64% acid concentration, with varying acid to fibre ratios, at temperatures around 45-50 °C, for 30-75 min duration under vigorous stirring. It typically produces needle-like structures, with the diameter and length in the range of 4–25 nm and 100–300 nm, respectively. This review analyses the results reported in the literature regarding the influence of hydrolysis parameters on the extraction of CNCs from various cellulosic materials. The study examines various hydrolysis parameters, specifically extraction time, temperature and acid concentration, to isolate CNCs with controlled morphology, crystallinity and thermal stability.

Keywords: cellulose nanocrystals, acid hydrolysis, sulphuric acid

INTRODUCTION

Lately, because of the depletion of fossil resources and alarming negative effects of conventional petroleum-based products on the environment, there has been an increasing interest in the utilization of renewable and biodegradable resources, such as cellulose.[1-5] Therefore, cellulose containing biomasses have become an alternative to fossil resources for chemical manufacture and fuel production. Cellulose is abundantly available in nature and exists in all plant cells. It is also found in living species that include bacteria, algae, fungi and tunicates. Structurally, cellulose is a linear syndiotactic homopolymer composed of α-D-anhydroglucopyranose units, which are linked by 1-4 glycosidic bonds. The polymerization degree of cellulose can reach up to 20000 glucose units in one chain, depending on the source of extraction. Wood has been traditionally used as a major source of cellulose fibers, until recently.

Various agricultural residues, such as rice straw, wheat straw, sugarcane bagasse, cotton stalk and bamboo wastes, are nowadays used to extract cellulose due to their lower cost, wide availability and renewability properties. The use of such agricultural residues as raw materials also brings some disadvantages, including the lack of heterogeneity of the raw material, and not easily reproducible experimental conditions. Moreover, it is difficult to purify them, remove the effluent efficiently and control product quality.

Cellulose nanocrystals (CNCs) extracted from non-wood cellulosic sources have attracted significant attention due to their numerous advantages, including non-toxicity, excellent mechanical properties and high surface areas.[6-12] In recent years, there have been increased efforts to scale up the processing and economy of CNCs isolation. For example, CNCs isolation in large scale production has been reported in Canada and the United States for potential utilization as reinforcement or functional additive in commercial products.[13] The impetus for this lies in the multitude of applications of CNCs in various fields, such as pharmaceuticals, cosmetics, food packaging, textiles *etc*.[14-17] It should be mentioned that there is a potential usage of CNCs as reinforcing filler and as nucleating agent for polymers, owing to their properties. The presence of abundant surface hydroxyl groups, high aspect ratio and excellent mechanical properties make them ideal for such applications.[18] For instance, Zhang *et al*.[19] used CNCs to enhance the crystallization of polylactic acid (PLA). Luzi and coworkers[20] reported an improvement in the barrier properties due to the combined nucleation effect of CNCs and polybutylene succinate (PBS) in the PLA matrix. Thomas *et al*.[21] observed significant improvements in the Young's modulus and tensile strength of the natural rubber nanocomposites reinforced with CNCs isolated from raw jute fibre. Similarly, an improvement in mechanical properties, as well as water barrier resistance, was also reported by Lani *et al*.[10] and Srivastava *et al*.,[22] with the introduction of CNCs into a polyvinyl alcohol/starch blend and polyvinyl alcohol, respectively.

The isolation of the CNCs from various cellulosic resources generally brings variability in thermal stability, structural dimensions, surface charge and crystallinity index. Arserim-Ucar *et al*.[23] also argued that the resultant yield depends on the cellulose source, hydrolysis conditions, including acid type and concentration, acid to pulp ratio, reaction time and temperature. In the literature, there are a number of reviews reported on the extraction and possible applications of crystalline nanocellulose.[24-28] This review synthesizes available information on the influence of acid hydrolysis parameters on the CNCs extracted from various cellulose biomasses. Factors such as hydrolysis time, temperature and types of acids used will be thoroughly investigated. The study focuses on attempts to isolate CNCs with controlled morphology, crystallinity and thermal stability, using various acids, including acid mixtures such as hydrochloric acid/sulphuric acid, amongst others.

ACID EXTRACTION

Various methods have been used over the years to prepare CNCs from native cellulose, which include acid hydrolysis, mechanical (high pressure homogenization and ultrasonication) and enzymatic methods. Among them, acid hydrolysis is the most preferred method, involving subjecting the cellulose fibre to concentrated acid to break the amorphous parts of the cellulose, and thus release well-defined crystals under controlled conditions of temperature, acid concentration, agitation and time. Different acids, such as sulphuric acid, phosphoric acid, hydrochloric acid, nitric acid, formic acid *etc*. have all been used, resulting in CNCs with different morphological, structural and mechanical properties.[29-31] Amongst all these acids, sulphuric acid hydrolysis is the most often used and requires shorter reaction time. Moreover, it gives the highest crystallinity index and dispersed nanocellulose as a stable colloid system due to the esterification of hydroxyl groups by sulphate ions. Sulphuric acid hydrolysis is generally performed with 64% sulphuric acid with varying fibre to acid ratio at temperatures around 45-50 °C for 30-75 min (see Table 1). This step is normally followed by dialysis and ultrasonic treatment before the obtained CNCs are neutralized by a base solution. However, many other procedures also exist in the literature to isolate CNCs using sulphuric acid hydrolysis.[32,33] During the hydrolysis process, sulphuric acid typically reacts with the hydroxyl to produce CNCs with inserted anionic sulphate groups and stable aqueous suspension that is negatively charged.[34,35] The presence of negatively charged groups promotes the formation of a negative electrostatic layer covering the nanocrystals and assists in the dispersion in water.

Similarly to cellulosic fibres, the abundant hydroxyl groups on CNC surfaces makes it a very hydrophilic material, which often weakens its excellent properties.[2] In general, the CNCs prepared by this method exhibit needle-like structure, with diameter and length in the range of 4–25 nm and 100–300 nm, respectively. The resultant yield and crystallinity index typically vary depending on the hydrolysis conditions and the cellulose fibre used.[36,37] The usage of sulphuric acid also has several drawbacks, such as low thermal stability of CNCs, equipment corrosion, large water usage and the generation of a large amount of salt for disposal, as well as acid wastes, which are difficult to recover and reuse.[38,39]

Hydrolysis using hydrochloric acid (HCl) and other inorganic acids, such as phosphoric acid (H_3PO_4), hydrobromic acid (HBr) and nitric acid (HNO_3), has also been reported in the literature. The CNCs isolated with these acids typically aggregate easily in most solvents or polymers due to the abundance of surface hydroxyl groups, which form strong intra- and intermolecular hydrogen bonding interaction.[4,40] On the contrary, CNCs obtained by sulphuric acid hydrolysis present negatively charged surface that promotes resistance to aggregation and the formation of stable suspensions.[41] Lefatshe *et al*.[8] successfully extracted CNCs with a crystallinity of 53.3% from oil palm empty fruit bunches using 30% HCl. Nagarajan *et al*.[38] extracted CNCs by means of citric acid hydrolysis at different concentrations (64 wt%, 76 wt% and 84 wt%). The obtained CNCs had relatively high thermal stability when compared to those achieved by sulphuric acid hydrolysis. Thomas *et al*.[21] subjected raw jute fibre to oxalic acid treatment, followed by steam treatment to produce CNCs. The study showed that a mild acid coupled with steam explosion helped in defibrillating the fibre to nano-range, as confirmed by SEM analysis. Liu *et al*.[42] extracted CNCs from corncob residue using formic acid and other methods. The main advantage of formic acid is that it can be recovered easily and causes less equipment corrosion. Yeganeh *et al*.[43] isolated CNCs from waste office paper using maleic acid and sulphuric acid. The obtained CNCs had different sizes, yields and crystallinity as a function of the acid used for hydrolysis. In another study, HNO_3 was also used to isolate CNCs from cellulosic fibre.[44]

Recently, the usage of a mixture of acids for the isolation of CNCs has been reported in numerous studies. Kassab *et al*.[45] isolated CNCs using hydrolysis with a citric acid/hydrochloric acid mixture. The obtained CNCs showed excellent properties as potential nano-reinforcing agents for polymer composites manufacturing. Zhang *et al.*[46] extracted rod-like CNCs by Fischer esterification with a mixed acid solution of HCOOH/HCl at 90 °C for 3 hours. Cheng *et al*.[40] isolated CNCs through a one-step hydrolysis process by using a mixed acid system of H_2SO_4/HNO_3. The isolated CNCs showed excellent dispersibility in several organic solvents that included ethanol. Chen *et al*.[47] isolated CNCs from bamboo fibre using a one-step HCOOH/HCl hydrolysis. The obtained CNCs showed improved thermal stability and crystallinity due to the introduction of formate groups. In another study, Vanderfleet *et al*.[33] studied the thermal degradation of CNCs isolated through acid hydrolysis using blends of phosphoric and sulphuric acid. Zhang *et al*.[48] compared different CNCs obtained from bamboo cellulose by hydrolysis with a mixture of acetic acid and nitric acid with sulphuric acid, hydrochloric acid and phosphoric acid. The results showed that the type of acid influenced the structure, morphology, and thermal stability of cellulose crystallites. In other studies, CNCs were extracted using mixtures of HCl/HNO_3,[46] HCl/H_2SO_4,[50] and H_3PO_4/HCl.[51]

Table 1
Hydrolysis parameters for various cellulosic biomasses

Source	H_2SO_4 (%)	Temperature (^oC)	Time (min)	Crystallinity (%)	Length (nm)	Diameter (nm)	Ref.
Cotton linter	65	45	45	86	150-250	10-20	6
Empty fruit bunch	64	45	45	73	120-200	4-15	10
Hemp fibres	64	45	30		140-180	4-6	20
Corn husk	64	45	90	83	135-200	23-30	29
Ushar seed fiber	64	45	75	70	140-260	14-24	36
Sugarcane peel	64	45	45	99	130-180	15-25	59

CNCs DIMENSIONS

CNCs extracted from different natural biomass resources possess a number of interesting features, including low cost, biocompatibility and biodegradability. Several studies have revealed that CNCs have large specific surface area, low density (1.6 gcm^{-3}), high modulus of elasticity (140–150 GPa) and high tensile stiffness (2–6 GPa). CNCs can also have a perfect crystalline structure (about 65%-95% crystallinity) and modulus that is close to the theoretical modulus of a perfect crystal.[6,21,32,40] In addition, numerous studies in the literature have shown that CNCs dimensions are influenced by the acid hydrolysis conditions and the source of cellulose, amongst others. For example, the study by Arserim-Ucar *et al*.[23] showed that increasing the temperature of hydrolysis (about 10 °C), for both sulphuric and hydrochloric acid treatment, resulted in a reduction in the length of nanocrystals. According to the authors, the temperature increase removed more of the amorphous region of the cellulose by hydrolysing the glycosidic bonds, and led to more crystalline regions with a decreased length. Maciel *et al.*[41] varied the concentration of sulphuric acid (50, 64 and 75%) to extract CNCs from industrial cotton waste. They found that the suspensions obtained with 60 and 64 wt% sulphuric acid showed almost similar dimensions, in particular the length. On the other hand, the suspensions prepared with 50 wt% of sulphuric acid showed fibres with bigger dimensions, which might be in microscale. Nagarajan *et al*.[38] isolated CNCs with various citric acid concentrations (68 wt%, 76 wt% and 84 wt%) at standard temperature and hydrolysis time. The results showed that with an increase in acid concentration to 76%, rod-like structured CNCs (76 wt%) were visible, with a little amount of agglomeration. However, when the concentration of citric acid was more than 76 wt%, CNCs had a more pronounced tendency to form aggregates, which were spherical in shape. Interestingly, in a study by Liu *et al*.,[42] the dimensions of CNCs produced by formic acid and sulphuric acid were compared. The results revealed that formic acid hydrolysis produced longer CNCs than the ones obtained by sulphuric acid hydrolysis. Also, it resulted in high crystallinity and thermal stability due to its preferential degradation of amorphous cellulose and lignin.

In a study by Kassab *et al*.,[45] the dimensions of CNCs obtained from a mixture of citric/hydrochloric acid were relatively smaller than those of CNCs hydrolyzed by sulphuric acid. The results were attributed to the strong acidity of the citric/hydrochloric mixture acid, which severely broke the amorphous domains of native cellulose, resulting in smaller dimensions (see Fig. 1). Moreover, the CNCs extracted by Zhang *et al*.[46] by Fischer's esterification method, with a mixed solution of acetic/hydrochloric acids, showed the length of 200-500 nm and the diameter in the range of 15-31 nm. These dimensions were greater than the ones obtained by a mixed acid system of sulphuric acid and nitric acid, with the length and diameter of 186 ± 13 and 9 ± 3 nm, respectively.[40] Interestingly, Martelli-Tosi *et al*.[37] compared the dimensions of CNCs derived from sulphuric acid and enzymatic treatment. The results showed that enzymatic treatment presented non-uniform lengths of agglomerated nanofibrils, whereas CNCs derived from acid hydrolysis were shorter with lengths ranging from 100 to 600 nm. The study confirmed that the length of nanocellulose is also dependent on the extraction method, *i.e*., chemical or enzymatic treatment.

CNCs YIELD

Hamid *et al*.[16] investigated the effect of ultrasonication power and time on the yield of nanocellulose in their study. The authors obtained the highest yield of nanocellulose (85%) when cellulose was exposed to mechanical treatment by ultrasonication under optimized conditions of about 225 W and 10 min. The authors explained that only the weak bonds of amorphous cellulose portions were broken and the cellulose inter-layers were partially disentangled at low sonication power. Moreover, the breakage of the strong glycosidic bonds in the crystalline portion of cellulose occurred at higher sonication power and reaction time, resulting in no increase in the yield. In another study, Silverio *et al*.[35] reported a decrease in yield with an increase in extraction time. The sulphuric acid hydrolyzed CNCs extracted at 30 min yielded 57% of the initial raw fibre, as compared to 50 and 46% yields at 60 and 90 minutes, respectively. Similar results were also reported by Chen *et al*.,[47] varying time from 2 h to 6 h. The study suggested that longer reaction time will hydrolyze smaller size CNCs, causing a reduction in the CNC yield. Furthermore, the increase in reaction time also results in a gradual decrease in both the length and diameter of CNCs. In another study[43] comparing the yield produced by maleic acid and sulphuric acid, the results

showed that rising the hydrolysis temperature (from 45 to 60 °C) in the maleic acid process improved the CNCs yield by 10%, as compared to the yield obtained by sulphuric acid. The authors related the increase in the CNCs crystallinity obtained with maleic acid with the improvement in the CNCs yield.

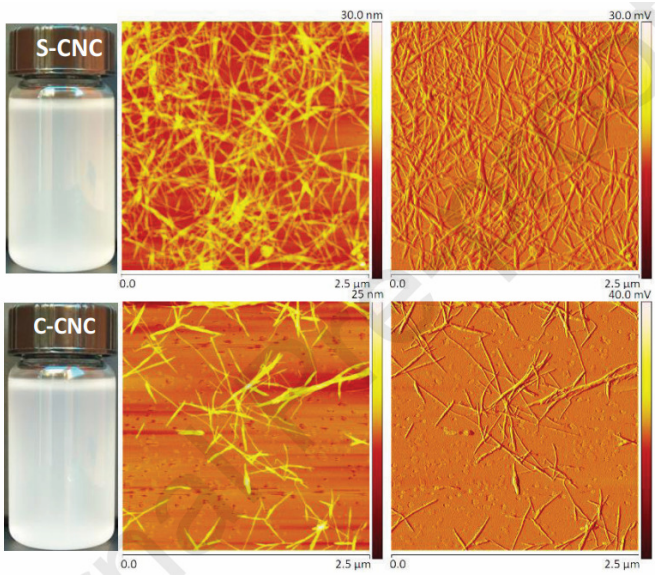

Figure 1: Aqueous suspensions and AFM images of sulphuric acid CNCs (top) and citric acid CNCs (bottom)[45]

The influence of an increasing acid concentration on the resultant yield was studied by Ji *et al*.,[51] while extracting CNCs using citric acid. The results showed that the yield was enhanced with an increase in citric acid concentration. The yield of CNCs obtained with 80% citric acid concentration was 2–5 times higher than that obtained with 60% concentration at the same temperature and time. The results were in line with those obtained by Zaki *et al*.,[52] and Rhim *et al*.,[53] who explained that an increase in the yield is dependent on the increase in sulphuric acid concentrations. Both studies showed that the maximum increase in the yield was obtained in the range 57-60%. In addition, lower concentrations of acids (39-45 wt%) and an increase in reaction time resulted in lower yield. Interestingly, Han *et al*.[54] obtained higher yield when extracting CNCs using sulphuric acid hydrolysis, as compared to high-pressure homogenization and high-intensity ultrasonication.

CRYSTALLINITY ANALYSIS

The effect of acid hydrolysis on the crystallinity index of cellulose has been studied by many authors using different methods. Generally, acid hydrolysis of native cellulose results in an increase in crystallinity index due to the removal of lignin, hemicelluloses and pectin after the treatment. Moreover, the crystallinity index largely affects the cellulose strength, stiffness and the amount of crystalline material in a cellulosic sample.[31] For instance, Oun *et al*.[36] observed an increase from 40 to 70% in the crystallinity index of the CNCs. They attributed this behaviour to the removal of amorphous regions from the cellulose fibres by sulphuric acid hydrolysis. Morais *et al*.[55] reported a higher crystallinity, of 90.4% from 60.4%, for CNCs extracted from cotton linter using sulphuric acid hydrolysis. Johar *et al*.[56] and Dassan *et al*.[56] attributed the crystallinity index increase to the dissolution of amorphous cellulosic domains caused by acid hydrolysis for extracting CNCs from rice husks and oil raw palm fruit bunch, respectively. Similar results were also reported by Maalolou *et al*.,[57] and Evans *et al*.,[58] extracting CNCs using sulphuric acid hydrolysis. During the chemical treatment, sulphuric acid reacts with the amorphous region of cellulose, causing hydrolytic cleavage of the glycosidic bonds, thus releasing individual crystallites. This in turn causes the growth of crystals, which contributes to the increase in crystallinity. According to Abiaziem *et al*.,[59] an increase in the crystallinity index (>70%) can be related to rising chemical and thermal stability, rigidity and bacterial resistance of the

material. In a study by Dasan *et al.*,[52] comparing the crystallinity index obtained using various acids, it was remarked that the CNCs prepared with hydrochloric acid and a mixed acetic acid/nitric acid solution possessed lower crystallinity than those obtained with sulphuric acid. The reason was related to their higher tendency to promote breakage of the hydrogen bonds in the crystalline regions of cellulose. On the other hand, Kassab *et al.*[45] reported a greater crystallinity index of CNCs hydrolyzed by a mixture of citric acid/hydrochloric acid (83%) than those hydrolyzed by sulphuric acid (81%) in their study.

Amongst other factors that influence the crystallinity index, hydrolysis parameters, such as acid concentration, temperature and time, should be included. Rhim *et al.*[53] investigated the influence of acid concentration of CNCs isolated from onion skin. It was apparent that the crystallinity index of CNCs extracted using acid concentration of 55% was greater than the index obtained at 65% concentration at a constant time (45 minutes). The increase in crystallinity of CNCs, as compared to that of the raw cellulosic material, was related to the hydrolysis of glucosidic linkages in the accessible regions of cellulose fibres.[53] Moreover, Yeganeh *et al.*[43] reported a decrease in crystallinity index with increasing temperature and time from 45 °C to 60 °C, and from 90 min to 120 min, respectively. On the contrary, there was an increase when maleic acid was used to hydrolyze CNCs, in the same study using similar conditions. When rising hydrolysis time using maleic acid, the hydronium ions penetrated amorphous regions of cellulose, promoting hydrolytic cleavage of glycosidic bonds and thereby releasing individual crystallites. Longer periods of hydrolysis are known not only to remove the amorphous region, but also to destroy part of the cellulose crystalline regions. This sentiment was clear in the findings by Silverio *et al.*,[35] who reported an increase in crystallinity index with an increase in hydrolysis time. The study showed that the sample hydrolysed for 90 minutes presented a decrease in crystallinity, compared to samples hydrolysed for 30 and 60 min.

Liu *et al.*[42] compared the crystallinity index of CNCs extracted from corncob using sulphuric acid, formic acid, oxidative and mechanical methods. The results showed that formic acid hydrolysis led to higher crystallinity, as compared to other acids. Formic acid was less aggressive than sulphuric acid in attacking the crystalline region of cellulose. The oxidation and mechanical method exhibited the lowest crystallinity of CNCs. The findings of the study indicated that the crystalline region is not vulnerable only to strong acid, but also to oxidation and mechanical methods. Yang *et al.*[29] compared the crystallinity index of CNCs extracted from corn husk using sulphuric acid hydrolysis (AH-NC), TEMPO oxidation (TO-NC) and ultrasonication (US-NC) in their investigation. The crystallinity index of AH-NC (83.51%) was followed by those of US-NC and TO-NC with 72.33% and 53.47%, respectively. The study explained that acid hydrolysis and TEMPO oxidation have potential to remove the non-cellulosic materials, while the high intensity ultrasonic treatment has no effect on the removal of non-cellulosic substances. In addition, the ultrasonic cavitation effect has no selectivity, acting on both crystalline and amorphous areas of cellulose and causing some damage to the crystalline regions. Other parameters, such as sonication power, were reported to affect the crystallinity of CNCs as well. Hamid *et al.*[16] showed that increasing the sonication power from 50 to 225 W resulted in an increase in crystallinity to 88% from 75.6%. The increase of the crystallinity index in this study was related to the reduction and removal of the amorphous region of cellulose under controlled sonication.

Crystallinity index is also affected by hydrolysis temperature, as observed in the study by Cheng *et al.*, [40] who extracted CNCs by mixed acid hydrolysis. There was an increase of 91.7% when increasing the temperature to 70 °C. The results indicated that the mixed acid hydrolysis treatment hydrolyzed the amorphous regions of cellulose more efficiently and converted the surface hydroxyl groups of cellulose into charged carboxyl groups. The study by Huntley *et al.*[44] found that the crystallinity index for the CNCs extracted from wheat straw was slightly higher for the nitric and sulphuric acids, when compared to hydrochloric acid. The authors related the changes in percent crystallinity for the acid extractions to the acid strengths, since the hydrolysis times were constant. Hence, based on pKa values, the order of acid strength was reported as follows: HCl > H_2SO_4> HNO_3. It was concluded that, as the strength of the acid decreases (HCl > H_2SO_4 > HNO_3), the percent crystallinity increases (HCl < H_2SO_4< HNO_3). These findings were supported by Zhang *et al.*,[48] who reported that the

crystallinity index obtained with the mixture of acetic and nitric acid was lower than that obtained by sulphuric acid and phosphoric acid, but greater than that reached by hydrochloric acid. The order of crystallinity index in ascending order was reported as follows: HCl, $COOH/HNO_3$, H_2SO_4 and HNO_3. Correa *et al.*[49] reported crystallinity index values of 79.10%, 78.45%, 73.85%, 78.92% and 78.68% for HCl, HNO_3, H_2SO_4, HCl/HNO_3 and HCl/H_2SO_4, respectively, as compared to microcellulose (79.50%). The lower crystallinity index for H_2SO_4 was related to the excessive cellulose degradation under H_2SO_4 hydrolysis, which removed the amorphous component and partly damaged the crystalline regions of the cellulose. Xiong *et al.*[60] also reported a lower crystallinity index for sulphuric acid hydrolysis in their investigation.

MORPHOLOGICAL STUDIES

To analyse the morphology and dimensions of CNCs, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analyses are frequently employed. TEM micrographs of CNCs extracted by acid hydrolysis typically show needle-like whitish suspensions, which can be individualized or agglomerated, with varying size according to hydrolysis parameters, such as acid concentration, time and temperature.[32,36] SEM images normally show changes in the morphology of fibres in terms of size and level of smoothness after acid hydrolysis. In a study by Evans *et al.*,[57] SEM micrographs revealed size reduction of fibre aggregates in alkali treated bleached fibre, compared to the raw fibres, with their irregular structure, with the presence of some residues. Also, the SEM image of acid hydrolyzed fibres confirmed the size reduction due to the removal of amorphous components, and the permanence of the crystal cellulosic portion. Maciel *et al.*[41] obtained CNC suspensions that were translucent, with clear evidence of nano-sized particles (64 wt%), as compared to the suspension obtained with the lowest acid concentration (50 wt%). The 50% sulphuric acid hydrolyzed suspension was milky white and showed precipitation, indicating the presence of large fibres and fibre aggregates. In another study by Morais *et al.*,[55] the nanocellulose suspension extracted with 60% sulphuric acid hydrolysis appeared whitish, and showed an agglomeration of nanocellulose bundles with dispersed crystallites and individual crystals.

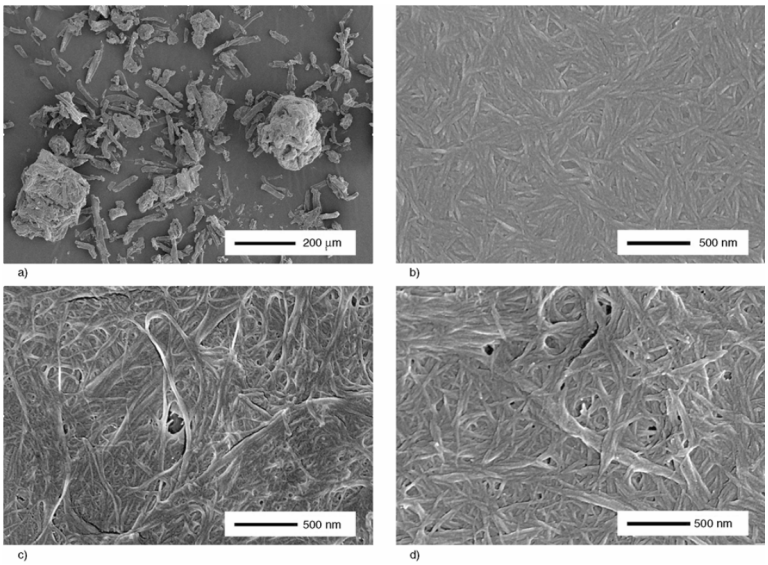

Figure 2: SEM images of (a) untreated cellulose, (b) sulphuric acid-derived nanocellulose, (c) TMO-derived nanocellulose and (d) nanocellulose obtained by ultrasonication [61]

Interestingly, in the study, the suspensions of nanofibers obtained by hydrolysis with HCl and a mixture of H_2SO_4/HCl were less stable than the suspension extracted using H_2SO_4 for hydrolysis. According to Correa *et al.*,[50] the incorporation of sulphate groups on the cellulose surface creates a negative electrostatic layer, resulting in a more stable final suspension. On the other hand,

hydrolysis with HCl and H_2SO_4/HCl yielded nanofibers with higher agglomeration. Moreover, the usage of only HCl as an acid for cellulose hydrolysis caused a tendency of nanocrystal agglomeration. This was caused by the lack of electrostatic repulsion charges among crystal particles, because chlorite ions were easily removed during the dialysis process. Differences in the morphology of untreated cellulose and CNCs isolated by sulphuric acid hydrolysis, TEMPO-mediated oxidation (TMO) and ultrasonication (US) in a study by Zhou *et al.*[61] are revealed by SEM images exhibited in Figure 2. Thus, CNCs isolated by the sulphuric acid technique have individual crystallites that disperse uniformly and present needle-shaped structures, whereas TMO-derived CNCs present interconnected webs with tiny nanofibrils with diameters of 40~80 nm and the lengths ranging from 200 nm to several micrometers. Moreover, the CNCs prepared by the ultrasonication treatment showed pieces of undefibrillated cellulose, with many microfibril bundles

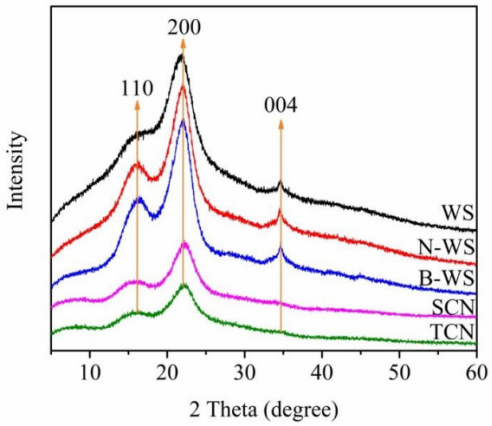

Figure 3: XRD patterns of WS, N-WS, B-WS, TNC and SNC[4]

Zheng *et al.*[4] investigated the morphological properties of TEMPO oxidation and sulphuric acid hydrolysis for walnut shell fibre. The XRD patterns showed that all the diffraction peaks remained unchanged following each treatment. The unchanged diffraction peaks indicated that the typical cellulose crystal structure was preserved following chemical and ultrasonic treatments. However, the crystallinity index of walnut shell changed after each treatment, leaving behind rod-like cellulose crystallites. Several studies reported that these peaks are observed at 2θ =14.8°, 16.6° and 22.9°, respectively (see Fig. 3). The peaks that appeared at 2θ of 22.8 and 18.0° typically represent the presence of crystalline cellulose and amorphous cellulose structure, respectively. Moreover, the intensity of CNCs peaks is generally much higher than in untreated cellulose, as acidic hydrolysis removes the amorphous regions of cellulose fibres.[3,43,62,63] The results were supported by the findings of Xiang *et al.*, [39] who also revealed that citric acid hydrolysis, with or without ultrasonication, had no influence on the position of peaks. Similarly, Zhou *et al.*[61] reported similar diffraction peaks for microcrystalline cellulose and CNCs extracted by acid hydrolysis, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated, oxidation and ultrasonication. In addition, Han *et al.*[54] showed that CNCs obtained via different preparation methods exhibited the characteristic cellulose I peaks, which indicates that acid hydrolysis, high-pressure homogenization, and high-intensity ultrasonication did not affect the main crystalline properties of cellulose.

THERMAL PROPERTIES

The thermal stability of the CNCs is also affected by the cellulose source, acid type and hydrolysis conditions, such as time, concentration of acid and temperature changes. The raw fibres, isolated cellulose and CNCs usually show two stages of weight loss when subjected to thermal degradation. The first stage is observed around 60-120 °C, depending on the type of cellulose, due to the evaporation of water. The second stage is observed around 200-400 °C and is caused by the thermal degradation of cellulosic materials.[23,29,56,64,65] Interestingly, Oun *et al.*[36] reported that sulphuric acid hydrolyzed CNCs

have a lower T_{onset} than cellulose, but higher onset than pure fibre, due to the presence of sulphate groups on the surface of the CNCs (Fig. 4). According to Arserim-Ucar *et al*.,[23] and Abiaziem *et al*.,[59] the amount of sulphate groups and residual acid from the hydrolysis procedure could be directly linked to the thermal stability of CNCs, and these sulphate groups catalyze the dehydration reaction by decreasing the decomposition temperature of sulphuric acid-treated CNCs. Generally, sulphuric acid hydrolysis leads to reduced thermal stability of CNCs, compared to neat fibres and their cellulose, by lowering the activation energy for the degradation of CNCs, and hence making the CNCs less resistant to pyrolysis. Additionally, the lower onset temperatures could be due to the smaller fibre dimensions, which lead to higher surface areas being exposed to heat, and partial disruptions of the crystal structure of cellulose.[42]

In other studies, Maciel *et al*.[41] reported that a decrease in sulphuric acid concentration might increase the thermal stability and decrease the number of degradation stages of CNCs. The authors observed that the hydrolysis conducted with 50 wt% sulphuric acid was not sufficient to provide an effective sulfonation. This was evidenced by the visual observation of suspension's stability and by the high values of dimensions and thermal stability. Ji *et al*.[39] also reported a reduction in the onset degradation and maximum loss temperatures with an increase in concentration and reaction time. The study attributed the reduced thermal stability to the smaller fibre dimensions that exposed larger surface areas to heat during hydrolysis, and accelerated the heat distribution. Rhim *et al*.[53] also reported a reduction in thermal stability with an increase in acid concentration in their study. The decrease in thermal stability of the CNCs was related to the introduction of sulphated groups into nanocrystals during the sulphuric acid hydrolysis of the fibre. The sulphate groups introduced onto the outer surfaces of cellulose caused dehydration of the cellulose fibre and reduced the thermal stability of the CNCs. The thermal stability of carboxylated CNCs was also lower than that of microcellulose after hydrolysis with mixed acids in a study by Cheng *et al*.[40] The reduction in the thermal stability was attributed to the smaller dimensions and the increase in the surface area. Moreover, the substitution of an unstable carboxyl group could also result in a decrease in thermal stability. The study also reported that the T_{onset} and T_{max} of carboxylated CNCs prepared at the reaction temperature of 80 °C increased by about 20.6 and 58.0 °C, respectively, compared to those for CNCs prepared by H_2SO_4 hydrolysis. The study by Yang *et al*.[29] compared the thermal stability of AH-NC, US-NC and TO-NC. The lower thermal stability was obtained for TO-NC, as compared to AH-NC and US-NC, was caused by the introduction of sodium carboxylate groups on the fibre surface during the TEMPO oxidation process. The sulphate groups on the surface of AH-NC can lower the activation energy of decomposition, which decreased the thermal stability of AH-NC. However, the study revealed that AH-NC has a compact structure and higher crystallinity index, which means a very small number of sulphate groups can be grafted to the surface of AH-NC.

The extracted CNCs hydrolyzed by a mixture of citric acid/hydrochloric acid in a study by Kassab *et al*.[45] showed very good thermal stability, comparable to that of native fibre and CNCs hydrolyzed by sulphuric acid. In this study, the T_{onset} of the acid mixture-derived CNCs and native fibre was obtained as 231 and 230 °C, respectively, as compared to the T_{onset} of 221 °C measured for sulphuric acid hydrolyzed CNCs. By contrast, the decomposition of CNCs extracted by sulphuric acid and phosphoric acid started at about 270 °C and reached a maximum at about 310 °C, whereas that of hydrochloric acid started at about 310 °C and reached a maximum at 342 °C. In a study by Zhang *et al*.,[48] the authors suggested that the CNCs obtained by sulphuric and phosphoric acids exhibited a slight decrease in thermal stability. In this work, the crystallinity index of sulphuric acid and phosphoric acid hydrolysed CNCs was higher than that of others. The introduction of sulphated groups and phosphorylated groups into the crystals during the acid hydrolysis process was related to the reduced thermal stability of nanocrystals. Accordingly, the CNCs isolated by sulphuric acid hydrolysis are known to degrade at lower temperatures than CNCs hydrolyzed with phosphoric acid. The thermal stability of CNCs increased with the usage of HCl or a mixture of H_2SO_4/HCl during hydrolysis.[33,50] Interestingly, Tarchoun *et al*.,[49] investigating the thermal stability of CNCs using various acids, showed that the decomposition onset temperature was the lowest for hydrolysis by sulphuric acid, as compared to other acids. The order of the decomposition was H_2SO_4 < HCl/H_2SO_4 < HNO_3 < HCl < HCl/HNO_3.

Moreover, the main degradation temperature followed the same order as the onset temperature, sulphuric acid and nitric acid extracted CNCs showing higher char content (see Fig. 5). Zheng *et al.*[4] also reported that, in comparison with commercial cellulose, HNO_3 and H_2SO_4 cellulose extracts revealed the greatest mass resistance to changes at temperatures near or above 300 °C. According to Huntley *et al.*,[44] comparing various acid hydrolyses, HCl leads to the greatest mass loss, while H_2SO_4 – to the least, in the higher temperature range. Also, HCl leads to a much faster rate of mass loss than HNO_3 or H_2SO_4. In addition, HCl causes the least residual mass, when compared to HNO_3, or H_2SO_4, but similar residual mass, when compared to that of commercial microcellulose.

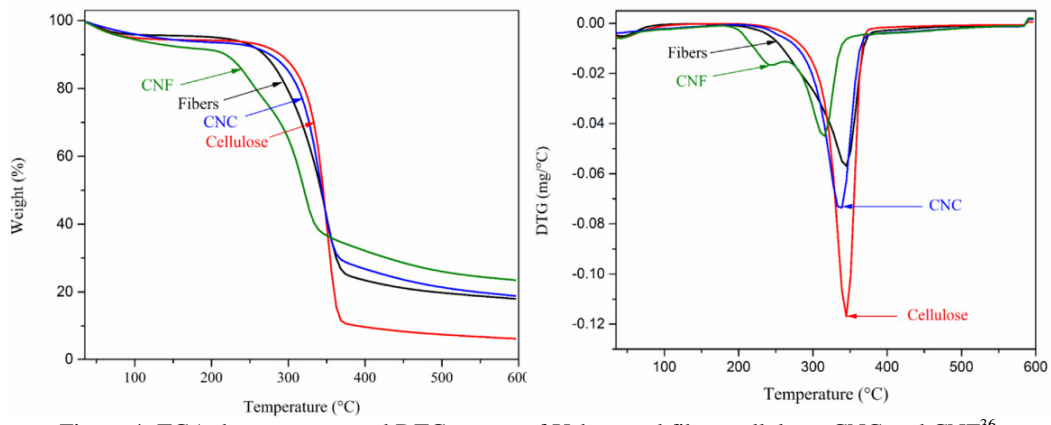

Figure 4: TGA thermograms and DTG curves of Ushar seed fibre, cellulose, CNC and CNF[36]

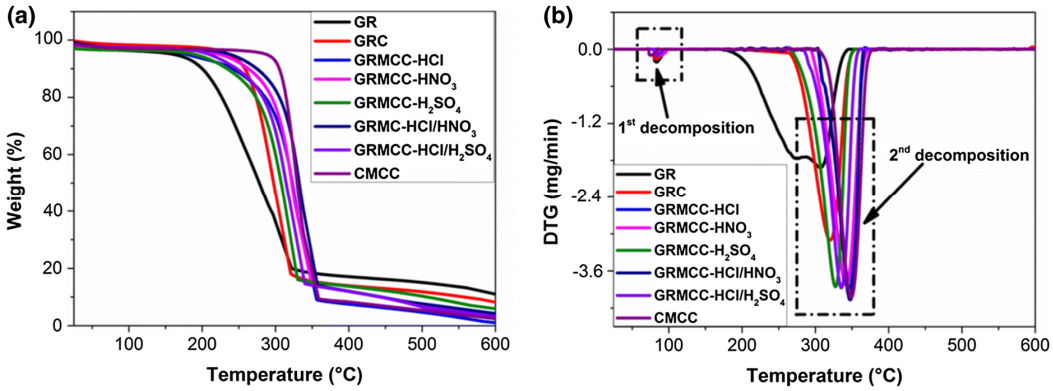

Figure 5: (a) TGA and (b) DTG thermograms of GR, GRC, GRMCC-HCl, GRMCC-HNO_3, GRMCC-H_2SO_4, GRMCC-HCl/HNO_3, GRMCC-HCl/H_2SO_4, and CMCC[49]

SUMMARY

It is clear from this literature review that acid hydrolysis is a very effective approach to isolating cellulose nanostructures. This method typically involves breaking the disordered and amorphous parts of the cellulose, thus releasing single and well-defined crystals under controlled hydrolysis conditions. Interestingly, various acids utilized for the hydrolysis are commercially readily available.[1,7,32] Acid hydrolysis generally yields needle-like morphologies, with diameters of 10-20 nm and lengths of several hundred nanometres. On the other hand, TEMPO-mediated oxidation, enzymatic hydrolysis and mechanical methods extract long flexible networks of fibrils, with the diameter in the nanoscale (5-110 nm) and length of a few micrometres.[27,29,37] Acid hydrolysis generally produces CNCs with greater crystallinity index, compared to other methods, including ultrasonication[54] and high-pressure homogenization,[29] though the yield might sometimes be lower. The yield might be improved by using a different approach to extract CNCs, such as high-pressure homogenization[66] amongst others. For example, Silverio *et al.*[35] obtained the yield of 79% and crystallinity index of 0.7 for CNCs extracted by acid hydrolysis, as compared to the yield of 98% and index of 0.59 for the

nanostructure obtained by TEMPO-mediated oxidation.

Acid hydrolysis does not require intensive energy consumption, as it is the case of mechanical methods, including ultrasonication, where the yield and crystallinity depend on the speed, duration and temperatures used. Moreover, it does not require longer reaction time, as it is the case of enzymatic hydrolysis, which can often take even weeks to reach completion.[16,42,52] The study by de Souza *et al*.[17] demonstrated that acid hydrolysis yielded smaller nanocellulose agglomerates, with better thermal stability than the mechanical method. This was evident by the higher T_{max} and initial decomposition temperature than those of the mechanical sample. Moreover, the CNC suspension isolated mechanically was not stable because of the deposition of aggregates. The suspensions resulting from acid hydrolysis are generally stable due to negatively charged surfaces.[2,5,42]

Even though acid hydrolysis displays a lot of advantages, it also presents several defects. It may be hazardous to the environment and human body, acids cause harsh corrosion to the process equipment, the process involves high water consumption and generates a large amount of salts and acid wastes for disposal. Also, as mentioned above, CNCs have a relatively lower thermal stability because of the introduction of sulphate groups. Moreover, the toxic acid fragments in the CNCs could lead to great potential risks when CNCs are applied in the production of other end-use materials, especially in food, cosmetics, pharmaceuticals and biomaterials areas.[1,24,39] However, research efforts are being made to diminish or avoid many of these disadvantages, for example, by using lower acid concentrations in combination with other treatments, such as steam explosion, as in the study by Thomas *et al*.[25] In the work by Alhamzani *et al*.,[67] acid hydrolysis followed by sonication resulted in nanocellulose with higher crystallinity and higher resistance to thermal degradation. Other researchers reported using supercritical water hydrolysis in the absence sulphuric acid,[68] or mild acids, such as lithium bromide trihydrate, to generate CNCs with a uniform size, higher yield and crystallinity.[69]

CONCLUSION AND RECOMMENDATIONS

In this review, the general effects of various hydrolysis parameters, such as temperature, acid concentrations and reaction time, on the resulting CNCs yield, morphology, crystallinity index and thermal properties were synthesized. Various methods and different acids, such as sulphuric acid, hydrochloric acid and nitric acid that can isolate CNCs from native cellulosic resources were reviewed. Acid hydrolysis using sulphuric acid has been found to be the preferred method, as it requires shorter time than most others and results in a higher yield of stable CNCs, with a lower tendency to form aggregates. Other types of acids, such as hydrochloric acid, citric acid and oxalic acid, typically require longer hydrolysis periods, diminishing some of the crystalline region of cellulose. The CNC dimensions, namely the length and diameter, are highly influenced by the extraction method and conditions. Amongst others, increasing the temperature of hydrolysis results in a reduction in the length of the CNCs for different types of acids studied. Acid mixtures typically result in smaller diameter and length, as compared to CNCs hydrolyzed by sulphuric acid. Considering different methods, enzymatic treatment and TEMPO oxidation generally produced CNCs with non-uniform lengths and more agglomerated compared to acid hydrolysis.

The yield obtained also depends on factors such as time period, concentration and isolation method used. Longer reaction time results in a reduction in yield and dimensions of CNCs. Moreover, the yield is enhanced with an increase in concentration for various acids. Generally, crystallinity decreased with an increase in acid concentration, temperature and time. The CNCs isolated by sulphuric acid hydrolysis showed higher crystallinity, compared to those obtained by TEMPO oxidation and ultrasonication. This review showed that nitric acid generally led to higher crystallinity compared to sulphuric acid, investigated at the same hydrolysis parameters. Sulphuric acid hydrolysis leads to reduced thermal stability of CNCs, compared with that of neat fibres and their cellulose, lowering the activation energy for the degradation of CNCs. However, the thermal stability of CNCs can be increased with the usage of HCl or a mixture of H_2SO_4/HCl during hydrolysis. There is generally a reduction in the onset degradation and maximum loss temperature with an increase in concentration and reaction time. CNCs hydrolyzed by HCl were generally more thermally stable compared to those obtained by sulphuric acid. Furthermore, lower thermal stability was obtained for TEMPO oxidation, compared to acid hydrolysis using sulphuric acid.

In conclusion, depending on the hydrolysis parameters used, it is possible to control the yield, morphology, crystallinity index and thermal properties of isolated CNCs, which thus allows obtaining materials with tailored properties for specific applications.

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