



## Solid Acid Hydrolysis for Isolation of Cellulose Nanocrystals and Chitin Nanocrystals – A mini review

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### Hidrolisis Asam Padat untuk Isolasi Selulosa Nanokristal dan Kitin Nanokristal – mini review

#### Abstrak

Selulosa dan kitin adalah dua biopolimer yang mempunyai ketersediaan paling melimpah di bumi. Kedua material ini telah menarik banyak minat dari banyak peneliti, terutama terkait dengan bentuk nanopartikelnya. Metode untuk mengekstrak menjadi bahan berskala nano sebagian besar dengan hidrolisis mineral atau asam cair, seperti asam sulfat dan asam klorida. Meskipun menghasilkan rendemen yang tinggi, terdapat banyak kerugian saat proses ekstraksi, seperti stabilitas termal rendah dan sulit untuk dimodifikasi gugus fungsinya karena adanya gugus sulfat, memiliki kecenderungan untuk teragregasi untuk hidrolisis dengan asam klorida, potensi degradasi selulosa yang berlebihan; adanya efluen dalam jumlah besar yang dihasilkan pada tahap netralisasi, dan adanya bahaya korosi pada peralatan dan lingkungan. Kelemahan-kelemahan tersebut dapat digunakan asam padat untuk isolasi selulosa nanokristal (CNC) dan kitin nanokristal (ChNC). Kemampuannya untuk mengkristal kembali dan dapat dihasilkan kembali membuat asam padat lebih ramah lingkungan. Kelebihan lainnya adalah sebagian besar asam dapat mengesterifikasi permukaan selulosa dan kitin, sehingga sangat layak untuk digunakan pada proses hidrolisis CNC dan ChNC. Tujuan dari makalah ini adalah untuk memberikan tinjauan kritis tentang kemajuan terkini terkait hidrolisis asam padat karena memiliki karakteristik yang menarik bahkan beberapa sifatnya lebih baik daripada metode konvensional.

Kata kunci: selulosa nanokristal (CNC), kitin nanokristal (ChNC), hidrolisis asam padat, esterifikasi

#### Abstract

Cellulose and chitin are two of the most abundant biopolymers on earth. These two materials have attracted a lot of interest from many researchers, especially related to the shape of the nanoparticles. Recently the method to extract them into nanoscale materials mostly by mineral or liquid acid hydrolysis, such as sulfuric and hydrochloric acid. Despite their high yield production, many disadvantages are produced by their use as a hydrolysis catalyst, such as low thermal stability and are difficult to be functionalized due to the presence of sulfate groups, tendency to be aggregated due to the bare surface charge density for hydrochloric acid hydrolysis, the potential excessive degradation of cellulose; and large amounts of effluent will be produced due to the neutralization stage and corrosion hazards to the equipment and environment. To overcome the drawback of those acids, solid acid can be used to produce cellulose (CNC) and chitin nanocrystals (ChNC). Its ability to re-crystallize and be regenerated makes it more environmentally friendly. Another advantage is that most of the acids can esterify the surface of cellulose and chitin which makes solid acids very suitable for use in CNC and ChNC hydrolysis processes. The purpose of this paper is to provide a critical review on recent progress related to solid acid hydrolysis since they have interesting characteristics even some of their attribute is better than the conventional method.

Keywords: cellulose nanocrystals (CNC), chitin nanocrystals (ChNC), solid acid hydrolysis, esterification

## Introduction

Nanomaterials, with any nanoscale outer dimensions, or with nanoscale internal or surface structures has already become a prominent area due to their unique physical and chemical properties resulting in improved performance and characteristics of final products in numerous end-user industries (Inshakova and Inshakov, 2017). Nanomaterials from bio-based resources have received a great deal of research interest in recent years as they are very likely to produce high-quality products with less environmental impact. The study of nanomaterials is not only about its extraction, but also the new applications in various fields. Among the nanomaterials, Cellulose Nanocrystals (CNC) and Chitin Nanocrystals (ChNC) are the most common representatives, which are green and sustainable nanomaterials derived from the natural most widely biomass. The type of nanomaterials extracted is determined by the processing methods: most of CNC and ChNC are extracted by chemical treatments, and cellulose nanofibrils (CNF) and chitin nanofibrils (ChNF) are produced by mechanical or chemical treatments. The dimension and crystallinity of CNC and CNF or ChNC and ChNF are the main differentiators. Most CNF and ChNF shape consist of mixtures of amorphous and crystalline cellulose chains with a length of up to several microns, while CNC and ChNC are highly crystalline shape with a length typically less than 500 nm (Moon *et al.*, 2011).

From a top-down perspective, cellulose and chitin contain crystalline and amorphous structures. These structures were formed by the aggregation of each of the structure chains via intra- and intermolecular hydrogen bonding. The crystalline phase of cellulose (CNC) and chitin (ChNC) can be separated from its amorphous phase by acid hydrolysis (Chen *et al.*, 2017). Both of the crystalline structures have been applied in the fields of pharmaceutical and biomedical engineering, food, sensor, paper and packaging, optical and electronic devices, and many more (Huang *et al.*, 2013; Jung *et al.*, 2015; Gopi *et al.*, 2017; Salaberria *et al.*, 2017). Many researchers have been used the mineral acid hydrolysis method to extract crystalline parts because this method has the highest yield compared to other methods such as mechanical treatment and enzymatic hydrolysis (Moon *et al.*, 2011; Song *et al.*, 2018). The mechanical method maybe can produce a 100% yield, but this method is not a selective method, it means both of the crystalline and amorph regions will be affected by the mechanical force, moreover a lot of CNF will

be formed during the process (Trache *et al.*, 2017; Xie *et al.*, 2018). The main shortcomings of this method are the potential excessive degradation of initial material, large amounts of effluent released from the neutralization stage process, and corrosion hazards of high concentration of strong acid to the equipment and environment (Chen, Xiaoquan Deng, Xueyan Shen, Wenhao, 2012; Amin *et al.*, 2015; Zhang, Tsuzuki and Wang, 2015). As an alternative, solid acids can be used to hydrolyze chitin and cellulose for sugar production with the advantage of easing acid recovery and the hydrolyzed materials can be functionalized with carboxyl groups (Chen *et al.*, 2016).

Many reviews summarized their source, chemistry, and applications of cellulose and chitin nanocrystals (Habibi, Lucia and Rojas, 2010; Duran, Paula Lemes and B. Seabra, 2011; Zeng *et al.*, 2012; Wan and Tai, 2013; Abdul Khalil *et al.*, 2016; Trache *et al.*, 2017; Xie *et al.*, 2018), but from our best knowledge, no review has been reported focused on the use of solid acid to prepare chitin and cellulose nanocrystals. The present review mainly focuses on the advances in preparation, properties, and potential application of CNC and ChNC by solid acid hydrolysis.

## The Structure and Extraction Method of Cellulose and Chitin Nanocrystals

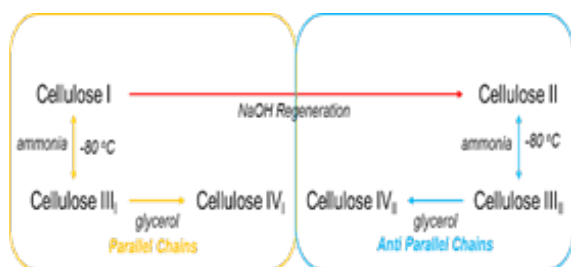
The structures of chitin and cellulose are very similar. Both are biological carrier and supporting materials in living plants and animals that grow in size from simple molecules in the nanometer range and composites in the micrometer range from highly crystalline fibrils (Fan, Saito and Isogai, 2008).

Cellulose, the most abundant biopolymer on earth have been attracted many researchers and industrial players in recent decades because of their excellent low toxicity, low density, biocompatibility, and biodegradability for numerous utilizations (Kargarzadeh *et al.*, 2018). The term “cellulose” and its molecular formula ( $C_6H_{10}O_5$ ) was first used in 1839 by Anselme Payen (Klemm *et al.*, 2005). It can not only be separated from many biomass resources such as wood, cotton, hemp, and other plant-based materials, but cellulose can also be synthesized by algae, tunicates, and some bacteria (Henriksson *et al.*, 2007; Iwamoto, Nakagaito and Yano, 2007; Siró and Plackett, 2010).

Cellulose can be described as a long linear polymer chain of ringed glucose molecules consisting of 1,4-anhydro-D-glucopyranose units and has a flat ribbon-like conformation (Siqueira, Bras and Dufresne, 2010; Dufresne, 2013).

Cellulose plays an important role in abundant organic raw materials. It can be used for different purposes all over the world in different stages including paper, composites, constructions, additives, pharmaceuticals, coatings, and many more (Li *et al.*, 2013; Lee *et al.*, 2014; Seabra *et al.*, 2018; Awang *et al.*, 2019; Lu *et al.*, 2019). The market demand for industry-based cellulose reached almost 350 million tons in 2013 and continues to grow by 2.7% a year.

Cellulose can be distinguished into four different polymorphs, those are cellulose I, II, III, and IV as shown in **Figure 1**. In its natural form, cellulose can be found both in the crystalline and amorphous phases of cellulose I. Infra-red spectroscopy and x-ray diffraction studies of cellulose organization in plants have shown that the crystalline regions have a bigger portion than the amorphous regions (Kroschwitz, 1985). The amorphous regions have lower density compared to crystalline regions and are easily available for bonding with other molecules, e.g. water. With the appropriate chemical hydrolysis method, cellulose microcrystals or nanocrystals (CMC/CNC) can be extracted from cellulose fibers. Meanwhile, if we use a mechanical method to handle cellulose fibers, mainly we could get micro or nano-fibrillated cellulose (CMF/CNF) (Siqueira, Bras and Dufresne, 2010). Cellulose II, or regenerated cellulose, is the most stable crystalline form obtained by regeneration of cellulose I with a strong alkali. The stable feature of cellulose II is mainly because of additional hydrogen bond per glucose residue and antiparallel layout atoms compare to cellulose I which has atoms direction in parallel shape (Saxena and Brown, 2005; Aulin *et al.*, 2009). Cellulose III is obtained by ammonia treatment of cellulose I and II, meanwhile, cellulose IV is produced by heating modification of cellulose III (Aulin *et al.*, 2009). **Figure 2** shows the basic chemical structure of cellulose, showing that a dimer called cellobiose appears as repeating segments. One monomer of cellulose contains three hydroxyl groups and these groups have the ability to form

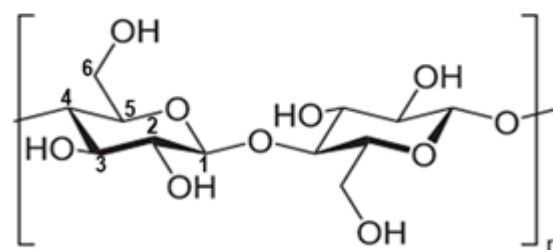


**Figure 1.** Polymorphs of cellulose (Panić *et al.*, 2013)

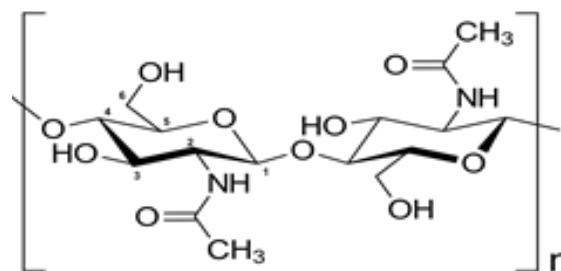
strong hydrogen bonds. Hydrogen bonds together with van der Waals forces form the basic cellulose fibers (Klemm *et al.*, 2011; Ng *et al.*, 2015).

After cellulose, chitin is the second most common biopolymer on the planet and is obtained from crab, shrimp, and lobster shell has been attracted wide usability due to the presence of the acetamido group on the second carbon of the pyranose ring (Barikani *et al.*, 2014; Salaberria *et al.*, 2017). As shown in **Figure 3**, Structure of chitin is a linear polysaccharide containing  $\beta$ -(1,4)-2-deoxy-2-acetamido-D-glucopyranose repeating unit (Goodrich, J. D.; Winter, 2007). An acetamido group (-NHAc) instead of a hydroxyl group at the C-2 positions of chitin distinguished chitin and cellulose (Duan *et al.*, 2018).

Chitin or poly ( $\beta$ -(1 $\rightarrow$ 4)-N-acetyl-D-glucosamine) was first proposed by Odier in 1823 as a material for insect cuticles. It kept its structure in outer shape after several treatments with a hot potassium hydroxide solution (Rudall and Kenchington, 1973). Chitin can be synthesized from many living organisms and in its natural form. Chitin is composed as structured crystalline microfibrils that form main structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast (Rinaudo, 2006). The degree of acetylation (DA) of chitin is typically around 0.90, indicating the presence of large amounts of 2-acetamido-2-deoxy-d-glucopyranose, which contributes to the presents of antimicrobial activity (Salaberria *et al.*, 2015; B. Duan *et al.*, 2018).



**Figure 2.** Molecular structure of cellulose ( $n$ =DP, degree of polymerization) (Visanko, 2015)



**Figure 3.** Molecular structure of chitin (Rodríguez *et al.*, 1989)

The crystalline phase, depending on its source, of chitin can be differentiated into  $\alpha$ ,  $\beta$ , and  $\gamma$  forms. All of them are assembled by the H-bonds network which controls the solubility, swelling, and reactivity (Younes and Rinaudo, 2015). The chain structure of  $\alpha$ -chitin is arranged alternately antiparallel, meanwhile, they are all parallel in  $\beta$ -chitin, and for the  $\gamma$ -chitin, it can be shown that two chains run in one direction and another chain runs in the opposite direction (Sugiyama *et al.*, 1999; Jang *et al.*, 2004). The  $\alpha$ -chitin occurs mainly in arthropods, fungi, and the cysts of Entamoeba,  $\beta$ -chitin is obtained from the pen of the Loligo squid,  $\gamma$ -Chitin exists in cocoon fibers of the Ptinus beetle and the stomach of Loligo (Jose and Alfredo, 1999).

$\alpha$ -chitin has strong hydrogen bonding between its layers, while  $\beta$ -chitin has weak intrasheet hydrogen bonding. That is the reason for  $\alpha$ -chitin has lower reactivity and dissolves in various solvents compare to  $\beta$ -chitin (Kurita *et al.*, 1993, 1994). For  $\gamma$ -chitin since Rudal and Kenchington (1973) proposed the invention, only a few investigations have focused on  $\gamma$ -chitin because of the unusual nature of the raw material. Kaya *et al.*, (2017) extract chitin from cocoon of the moth (*Orgyia dubia*) and they found that  $\gamma$ -chitin has different physicochemical characteristics, yet closer in structure to  $\alpha$ -chitin than  $\beta$ -chitin.

Renewable polysaccharides such as cellulose and chitin which are composed of crystalline and amorphous domains are candidates for organic nanoscale materials. The amorphous domains can be eliminated under certain methods such as acid hydrolysis, allowing the crystalline domains with high modulus can be extracted in nanoscale. The resulting nanocrystals can be used for many purposes such as nanocomposite, drug delivery system, waste removal, etc.

Cellulose nanocrystals are nanoparticles that can be derived from many sources such as, cotton (Sun *et al.*, 2016; Chen *et al.*, 2019; Ling *et al.*, 2019), wood (Beck-candanedo, Roman and Gray, 2005; Filson and Dawson-Andoh, 2009; Abushammala, Krossing and Laborie, 2015; Miao *et al.*, 2016), bamboo (Brito *et al.*, 2012; Yu *et al.*, 2012; Cao and Liu, 2015; Hong, Chen and Xue, 2016), tunicate (Zhao *et al.*, 2015; Cao *et al.*, 2017; Tang *et al.*, 2017), wheat straw (Oun and Rhim, 2016; Liu *et al.*, 2019), corn (Huang *et al.*, 2017; Liu *et al.*, 2019), fruits (Chieng *et al.*, 2017; Trilokesh and Uppuluri, 2019), and ramie (Grishkewich *et al.*, 2017; Kusmono, Wildan and Ilman, 2019). The origin of cellulose will determine the dimensions of CNC. For example, CNC derived from hardwood possess a dimension of 3 - 5 nm in diameter and 100 - 300

nm in length, whereas CNC extracted from tunicate have a lateral and length dimension of 15 - 30 nm and 1000 - 1500 nm respectively (Elazzouzi-Hafraoui *et al.*, 2008; Peng *et al.*, 2011). Meanwhile, chitin nanocrystals can result from many resources such as crab (Gopalan Nair and Dufresne, 2003; Kiruba *et al.*, 2011), shrimp (Einbu, 2007; Goodrich, J. D.; Winter, 2007), squid (Kurita *et al.*, 1994), and riftia (Morin and Dufresne, 2002; Perrin *et al.*, 2014), each of them has a different dimension in the range of 10 - 50 nm in diameter and 150 - 2200 nm in length (Paillet and Dufresne, 2001; Morin and Dufresne, 2002; Lu, Weng and Zhang, 2004; Phongying, Aiba and Chirachanchai, 2007). The first method for preparing a suspension of chitin nanocrystals happened in 1959 by Marchessault *et al* (Marchessault, Morehead and Walter, 1959). In this process, 20 g of purified chitin was refluxed in a 2.5N hydrochloric acid (HCl) solution for 1 hour, and the resulting hydrolyzed chitin was dispersed in rod-shaped particles and concentrated in the liquid crystal phase.

In recent years, several methods have been investigated for the isolation of CNC and ChNC, they are, chemical acid hydrolysis (Lahiji *et al.*, 2010; Li-rong *et al.*, 2011; Wang *et al.*, 2012; Yu *et al.*, 2013; Liu *et al.*, 2018; Xie *et al.*, 2019), enzymatic hydrolysis (Chen *et al.*, 2012; Xu *et al.*, 2013; Anderson *et al.*, 2014), mechanical refining (Amin *et al.*, 2015; Y. Li *et al.*, 2016), ionic liquid treatment (Tan *et al.*, 2015), subcritical water hydrolysis (Novo *et al.*, 2016), oxidation method (Fan, Saito and Isogai, 2008; Visanko *et al.*, 2014; Istomina *et al.*, 2019) and combined processes (Li, Wang and Liu, 2011; Phanthong *et al.*, 2015; An *et al.*, 2016; Jiang *et al.*, 2018; Seta *et al.*, 2020). Among those processes, acid hydrolysis is the most commonly used to produce nanomaterials, especially ChNC (Moon *et al.*, 2011; Zeng *et al.*, 2012) because of their simplicity, high crystallinity product, and high yield ability. Theoretically, acid aqueous solutions can hydrolyze the amorphous and crystalline domains of polysaccharides structures. The main function of acid catalysis during CNC and ChNC production is to hydrolyze and release the amorphous structure. This acid hydrolysis process will release hydronium ions for hydrolytic cleavage of glycosidic bonds in cellulose molecular chains within amorphous regions along the cellulose fibrils (Ng *et al.*, 2015).

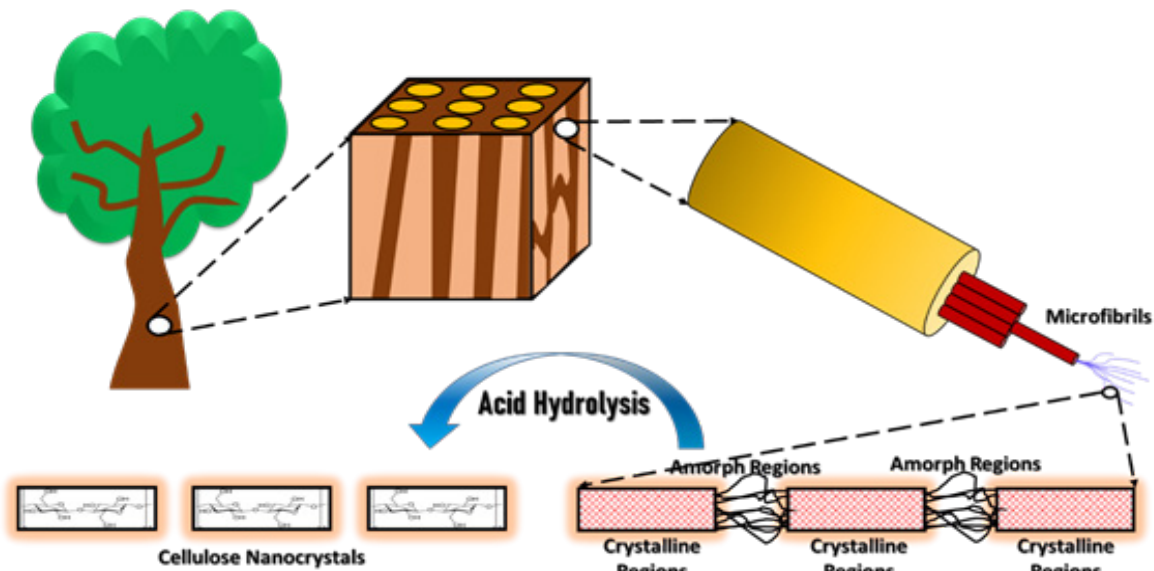
As shown in **Figure 4** and **Figure 5** The main principle for making nanocrystals of chitin and cellulose is based on the different kinetics of hydrolysis between them and the acid. Acid concentration and hydrolysis time are the most



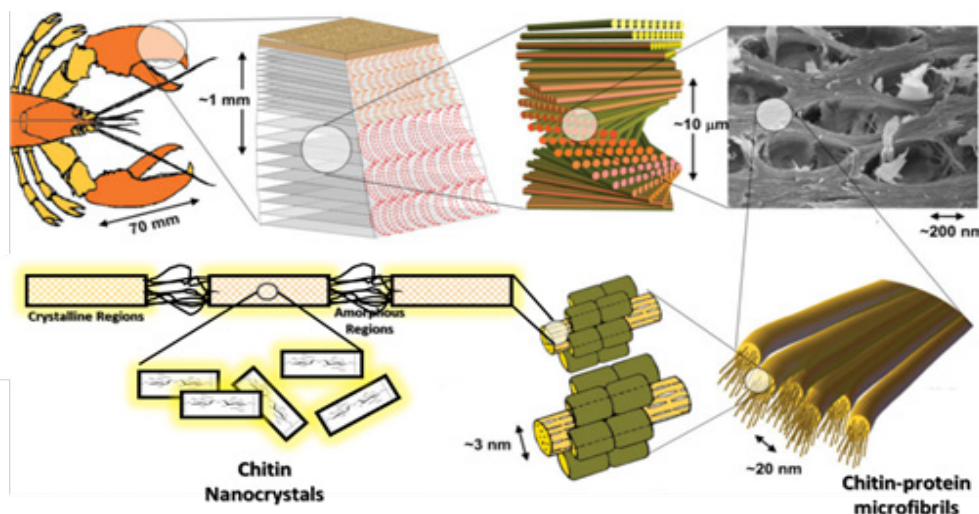
important factors in determining the particle size and yield of nanocrystals. The swelling and hydrolysis of the amorphous phase occur much faster than the crystalline phase due to the periodic proximity of the molecular chains within the crystalline domain. This is why controlling hydrolysis variables is so important to produce nanocrystals of the desired dimensions and good yield (Zeng *et al.*, 2012). The shape of the particles, the degree of crystallinity, and the size of the crystalline fibers depend on the natural source of the material and the method of extraction.

Mineral acid hydrolysis is one of the early developed and widely used to isolate and prepare CNCs and ChNCs. At present, primarily mineral

acids, such as sulfuric acid for CNC and hydrochloric acid for ChNC are usually used for the isolation nanocrystals. Sulfuric acid is the most typically used to extract CNC. In recent years a lot of articles have been published from 2010-2020 as we can see from **Table 1**. Regarding the market visibility to fulfill larger quantities of industrial needs, sulfuric acid is more suitable than hydrochloric acid. In 2008, sulfuric acid was the most widely produced chemical in the United States, almost 10 times more than hydrochloric acid (Börjesson and Westman, 2015). Sulfuric acid produces a negative surface charge on the particles, leading to a more stable suspension. In general, the hydrolysis process requires a sulfuric acid concentration of 60-65%,



**Figure 4.** Schematic illustration for the preparation process of cellulose nanocrystals (CNC)



**Figure 5.** Schematic illustration for the extraction method of chitin nanocrystals (ChNC) (Nikolov *et al.*, 2010)

a reaction temperature of 40-50°C, and a reaction time of 30-60 minutes. Some of those research results are shown in **Table 1**.

Unlike sulfuric acid hydrolysis, a lot of publications used hydrochloric acid to extract chitin nanocrystals. Meanwhile, many researchers prefer to use sulfuric acid than hydrochloric acid because this acid can make CNC very easy to be agglomerated in an aqueous system, because of the presence of less negative charge groups on its surface (Shang *et al.*, 2019). Hydrochloric acid has a high ability to swell chitin and cellulose, making it easier to break intramolecular and intermolecular hydrogen bonds in the crystalline region. Some of the researches that used this acid can be seen in **Table 2**.

**The CNC and ChNC isolation derived from different solid acid hydrolysis**

Despite the advantages of liquid and mineral acid hydrolysis, there are some drawbacks of this acid hydrolysis, are 1) it has low thermal stability and is difficult to be functionalized due to the presence of sulfate groups (for sulfuric acid-induced nanomaterials); 2) it tends to be aggregated due to the bare surface charge density (for hydrochloric

acid-induced nanomaterials) (Yu *et al.*, 2013); 3) the potential excessive degradation of cellulose; and 4) large amounts of effluent will be produced due to the neutralization stage and corrosion hazards to the equipment and environment (Chen *et al.*, 2016). To overcome these problems, solid acid instead of liquid acid can be used as a catalyst in the hydrolysis process considering its advantages: 1) highly safe for the storage; 2) low transportation cost; 3) more environmentally friendly; 4) caused less corrosion to process equipment; and 5) possible surface modification during hydrolysis (Yeganeh, Behrooz and Rahimi, 2017; Seta *et al.*, 2020). Some of the solid acids such as oxalic, maleic, and phosphotungstic have been reported can be used to produce nanomaterials. Most of the acids have the advantage of donating carboxylic structure and stability, the mechanism of the hydrolysis according to the structure is 1) maleic acid molecules react with β-1,4-glucosidic linkages/hydrogen bonds between anhydroglucose units in cellulose and chitin chains and release small and uniform particle size; 2) the acid can hydrolyze the disordered regions of materials to release the crystalline region; and 3) the acid can catalyze the esterification process of hydroxyl groups on the exposed chains and produce carboxylated CNC and ChNC.

**Table 1.** Cellulose and chitin nanocrystals prepared by sulfuric acid hydrolysis from different origins

Nanomaterials	Raw Materials	Conditions	References
CNC	Soy hulls	40°C, 30 or 40 minutes, H <sub>2</sub> SO <sub>4</sub> 64%	Flauzino Neto <i>et al.</i> (2013)
	Tea Leaf Waste Fibers	45°C, 45 minutes, H <sub>2</sub> SO <sub>4</sub> 65%	Rahman <i>et al.</i> (2017)
	Jackfruit peel	37°C, 1 hour, H <sub>2</sub> SO <sub>4</sub> 65%	Trilokesh and Uppuluri (2019)
	Cotton/ Cotton Linter	45-55°C, 5-25 minutes, H <sub>2</sub> SO <sub>4</sub> 50-64%	Chang <i>et al.</i> (2010); Morais <i>et al.</i> (2013); Sun <i>et al.</i> (2016); Csiszár and Nagy (2017)
	Flax	45°C; 25, 240 minutes, H <sub>2</sub> SO <sub>4</sub> 64%	Cao <i>et al.</i> (2008, 2013); Csiszár and Nagy (2017)
	Wood	35-80°C, 30-240 minutes, H <sub>2</sub> SO <sub>4</sub> 46-68.4%	Bondeson, Mathew and Oksman (2006); Durán <i>et al.</i> (2011); Wang, Zhao and Zhu, (2014); Beltramino <i>et al.</i> (2016); Dong, Bortner and Roman (2016); Lin, Enomae and Chang (2019); Kandhola <i>et al.</i> (2020)
	Sisal Fibers	45°C, 30 minutes, H <sub>2</sub> SO <sub>4</sub> 60%	Morán <i>et al.</i> (2008)
	Bamboo	30-60°C, 12-120 minutes, H <sub>2</sub> SO <sub>4</sub> 45-75%	Brito <i>et al.</i> (2012); Yu <i>et al.</i> (2012); Chen <i>et al.</i> (2013); Hong, Chen and Xue (2016); Wijaya <i>et al.</i> (2019)
ChNC	Crab Shell	60°C, 60 minutes, H <sub>2</sub> SO <sub>4</sub> 64%	Oun and Rhim (2018)
	Shrimp Shell	60-100°C, 90-180 minutes, H <sub>2</sub> SO <sub>4</sub> 64%	Gopi <i>et al.</i> (2017); Oun and Rhim, (2020)
	Lobster Shell	60°C, 90 minutes, H <sub>2</sub> SO <sub>4</sub> 64%	Li <i>et al.</i> (2016)

**Table 2.** Cellulose and chitin nanocrystals prepared by hydrochloric acid hydrolysis from different resources

Nanomaterials	Raw Materials	Conditions	References
CNC	Wheat Straw	24 hours, HCl 32%	Huntley <i>et al.</i> (2015)
	Cotton/ Cotton Linter	12 hours, HCl 35%	Lorenz <i>et al.</i> (2017)
	Wood	110°C, 90-180 minutes, HCl 37%	Cheng <i>et al.</i> , 2017; Shang <i>et al.</i> (2019)
	Filter Paper	110°C, 90 minutes, HCl 37%	Boujemaoui <i>et al.</i> (2015)
	Bamboo	60°C, 120 minutes, HCl 37%	Zhang <i>et al.</i> (2014)
ChNC	Crab Shell	80-100°C, 90 minutes, HCl 3M	Gopalan Nair and Dufresne (2003); Lu, Weng and Zhang, 2004; Tzoumaki, Moschakis and Biliaderis (2010); Goetz <i>et al.</i> , (2016); Jalvo, Mathew and Rosal, (2017)
	Lobster Shell	100°C, 90 minutes, HCl 3 M	Salaberria, Labidi and Fernandes (2014)
	Shrimp Shell	90-95°C, 90 minutes, HCl 3 M	Goodrich and Winter (2007); Perrin <i>et al.</i> (2014); Tzoumaki <i>et al.</i> (2015); Singh <i>et al.</i> (2020)
	Squid Pen	90°C, 90 minutes, HCl 3 M	Paillet and Dufresne (2001)
	Riftia Tubes	90°C, 90 minutes, HCl 3 M	Morin and Dufresne (2002)

### Oxalic acid

Oxalic acid is a dicarboxylic organic acid compound with the formula  $C_2H_2O_4$ , which has appearance as a white crystalline solid and forms a colorless solution in water, because of its appearance some people call it “crab acid”. It is an inexpensive chemical and can industrially be produced from plant-based resources and its melting point is around 104–106°C. Oxalic acid is industrially produced in three main ways: oxidation of different agricultural carbohydrate waste products (corn cobs, sawdust, oat hulls, etc.); fermentation processes caused by by-products in citric acid production; and pyrolysis of inorganic formats. This dicarboxylic acid finds many uses in the textile and leather industries and as an intermediate in organic syntheses (Sneeden, 1982). They dissolve in from 8 to 11 parts of water at 15.5°C and completely dissolve in water at 100°C (Hussain, 2012).

### Oxalic acid hydrolysis for the isolation of CNC

Chen *et al* (2016) used oxalic acid at a concentration of 50-70 % and 90-120°C for the first time to produce cellulose nanocrystals from bleached eucalyptus kraft pulp. The CNC has good dispersion and contains carboxylic acid group content of about 0.1–0.4 mmol/g. Thermal degradation temperature until CNC can reach 322°C. The crystallinity index

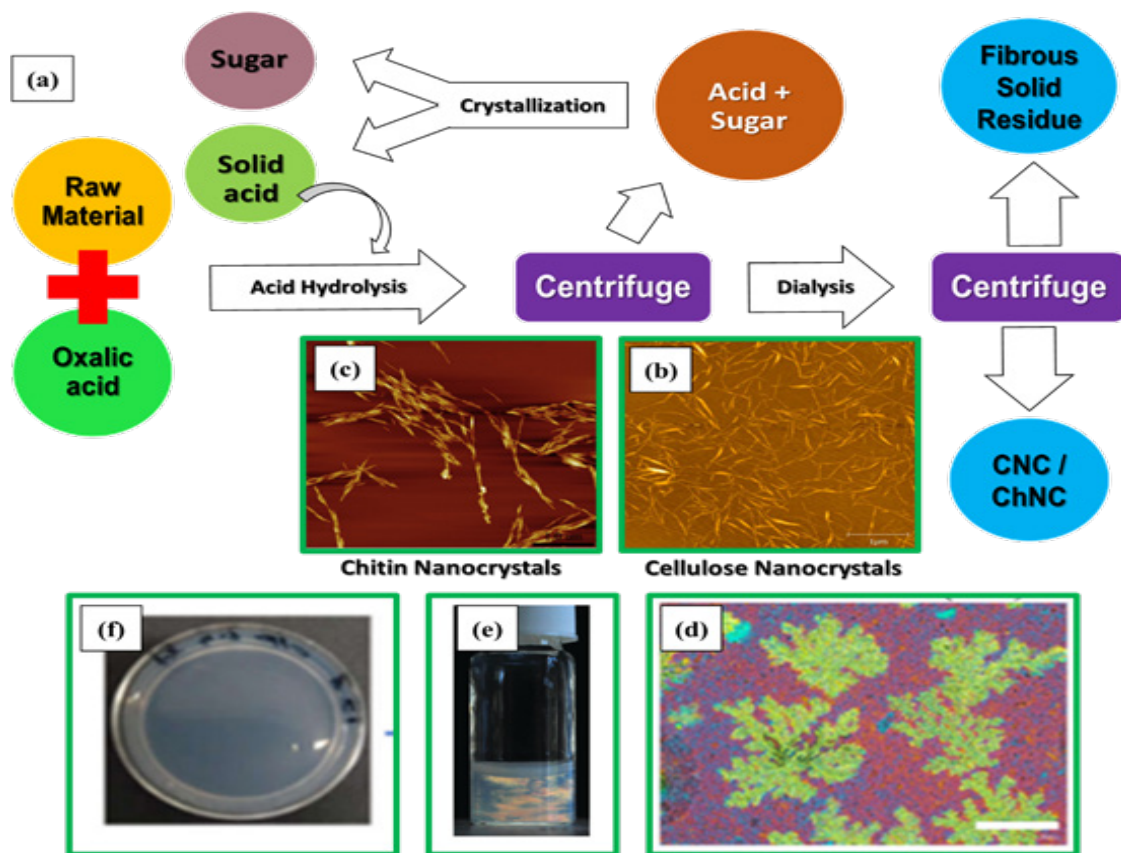
(CrI) was approximately 81%. The diameters of the CNC were approximately 15 nm and the shortest length was 273 nm. Xu *et al* (2017) also used oxalic acid at concentration 0.11-1.11 mol/L and hydrolysis temperature 80–100°C to hydrolyzed bleached birch kraft pulp. The resulted yield was about 85%. Maximum thermal degradation was 355°C, higher than CNC made by sulfuric acid hydrolysis (200°C). The obtained diameter was 8-15 nm, length 200-1200 nm, and carboxylic groups content was 0.1-0.3 mmol/g. The route of ChNC and CNC made by oxalic acid hydrolysis can be seen in **Figure 6(a)** and the resulted CNC and ChNC in **Figure 6(b)** and **Figure 6(c)**.

Li *et al* (2017) used softwood dissolving pulp and mixed it with oxalic acid at 110°C for about 15-120 minutes resulted CNC which has an average length of 150–220 nm and a width of 16–20 nm. Interestingly the yield of this method with 30 minutes hydrolysis time could reach 99%. This result was very high indicated that the use of oxalic acid can be an effective catalyst to hydrolyze cellulose into CNC. **Figure 6(e)** shows one of their research results was crossed polarized in an aqueous solution that can be used in the next nano-sized function. Another experiment was conducted by Xie *et al* (2019), they use bleached eucalyptus kraft pulp and mixed oxalic acid with sulfuric acid to reduce temperature (80°C) and increase yield (>70%). CNC has a diameter range

of about 5-20 nm and a length of 150-400 nm. The use of sulfuric acid could be reduced from 55 g/g CNC into 2.4 g/g CNC and 91±2% of oxalic acid can be reobtained by simple recrystallization. Song *et al* (2018) produced CNC by ball mill as a pre-treatment before hydrolyzing cellulose in various concentrations of oxalic acid. The optimum yield (±60%) was obtained by 60% oxalic acid, 80°C hydrolysis temperature, and 4 hours hydrolysis time. This hybrid process could extract CNC with good properties, such as maximum degradation temperature of 332 °C, 300-400 nm in length, and crystallinity index around 70.7%. Jia and Liu (2019) compared oxalic acid and sulfuric acid straightly. The filter paper was their raw material. The optimum condition of oxalic acid hydrolysis was 8.75% oxalic acid solution, reaction time 15 minutes, and temperature 110°C. In this condition they can get 93.77% of yield and they reported that the result was higher than previous researches. The conclusions of their work were oxalic acid CNC and sulfuric acid CNC have similar basic structural properties, such as UV-Vis transmittance, average

particle size, Zeta potential, and Crl value. But, as we can see in **Figure 6(d)**, they also found that the brilliant snowflake-like pattern of CNC film was observed through oxalic acid instead of sulfuric acid, and carboxylated CNC produced with oxalic acid easily forms a liquid crystal phase. Moreover, they suggested potential application prospects in optical devices and chiral separation according to its CNC properties.

Jia *et al.* (2017) compared three different raw materials and reacted with this dicarboxylic acid. They were used bleached eucalyptus pulp (BEP), spruce dissolving pulp (SDP), and cotton-based qualitative filter paper (QFP) as their raw research materials. The highest yield obtained by QFP (5.81%) with 50% oxalic acid solution was used at 100°C, 300 rpm, and 1 hour reaction time. The same group tried to increase the yield by adding disk milling (DM) pretreatment of bleached kraft eucalyptus pulp (Jia, Bian, *et al.*, 2017). They succeed increased it from 5% to 35% as shown in **Figure 6(f)**. The CNC was applied as film and 3D printed patterns. The prepared film produced via hybrid DM-oxalic



**Figure 6.** (a) Schematic diagram of oxalic acid hydrolysis (Chen *et al.*, 2016) (b) AFM Image of CNC (Chen *et al.*, 2016) (c) AFM image of ChNC (Yuan *et al.*, 2020) (d) POM images of CNC composite film (Jia and Liu, 2019) (e) A concentrated aqueous suspension of CNC observed between crossed polarizers (Li, Henschel and Ek, 2017) (f) The photo of CNC composite film (Jia, Chen, *et al.*, 2017)



acid method has very high transmittance and super low haze with great values of 90.6% and 6.6% at the wavelength of 600 nm. The prepared film can hold and maintain its appearance without visible change at 150°C for 4 hours. This characterization makes it very promising as electronic devices fabrication. The resulting 3D printing with porous structures shown this material can be potentially applied in tissue engineering scaffolds.

### Oxalic acid hydrolysis for the isolation of ChNC

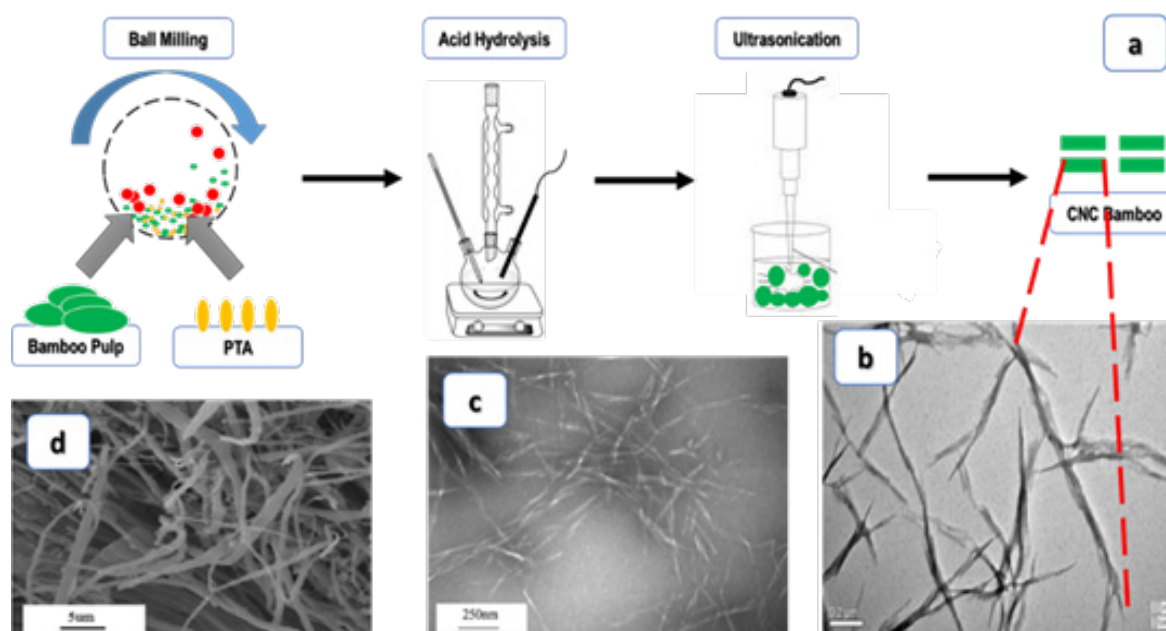
The use of oxalic acid to produce chitin nanocrystals was introduced by Yuan *et al* (2020). They mixed oxalic acid with choline chloride under mixing treatment at 100°C for 1 hour and 3 hours. The highest yield reached 79.5% and the morphology of ChNC was 530±89 nm in length and 49±8 nm in diameter. The crystallinity index could reach 90.09% and the temperature at maximum degradation was 367.2°C

### Phosphotungstic acid (PTA)

Phosphotungstic acid (PTA) is odorless acid and one of the strongest heteropoly acids with the chemical formula  $H_3PW_{12}O_{40}$ . Its melting point is 89°C and the solubility is 200 g/ 100 ml in water. As a heteropoly acid, PTA has some advantages, such as (1) high activity, thermal stability, and selectivity; (2) high solubility in polar solvents; (3) very high

proton mobility of heteropolyacid anions (Qiang *et al.*, 2016). Shimizu *et al* (2009) demonstrated that phosphotungstic acid has abundant Bronsted acid sites which can break the  $\beta$ -1, 4-glycosidic bonds in cellulose and could hydrolyze cellulose into glucose.

The use of PTA as a chemical in cellulose hydrolysis introduced by Liu *et al* (2014). They used bleached hardwood pulp as raw material and 50-85% of PTA mixture for 15-30 hours of hydrolysis time and 90°C of hydrolysis temperature. The optimum condition was obtained at 90°C for 30 hours by the use of 75% (w/w) PTA, the dimension of rod-like CNC was 15-25 nm in width and 600-800 nm in length as shown in **Figure 7(b)**. The crystalline index of CNC was 85% and maximum degradation has happened at 350°C. In this experiment, they recycled the PTA residue after the hydrolysis process and after 5 cycles the yield of the CNC could reach 58%, which was very close to the maximum yield of the regular process (60%). A higher yield can be obtained to extract a larger dimension. Qian *et al* (2016) tried to extract microcrystalline cellulose (MCC) from eucalyptus kraft dissolving pulp. The MCC has yielded of around 93.62%, length of 13.77–26.17  $\mu$ m, and crystallinity of 76.37%. They used 58 % (w/w) HPW catalyst and a solid-liquid ratio of 1:40, under the reaction condition at 90 °C for about 2 hours. From both experiments, we can see that the reaction time and solid-liquid ratio of acid mixture very determined the resulting nanomaterials.



**Figure 7.** (a) Schematic diagram of phosphotungstic acid hydrolysis simultaneous mechanochemical activation (Lu *et al.*, 2016) (b) AFM image of resulted CNC (Liu *et al.*, 2014) (c) AFM image of resulted CNC (Lu *et al.*, 2016) (d) SEM image of pristine bamboo (Lu *et al.*, 2016)

Lu *et al* (2016) used mechanochemical to extract CNC from bamboo pulp. From **Figure 7(d)**, bamboo pulp along with 12.5 % PTA solution were milled by 20,6 mm agate balls in an agate jar for 1.5-2.5 hours. Then, after removing agate balls from agate jar, the pulp and PTA solution were introduced into a round-bottomed flask which was kept the temperature at 90 °C in an oil bath for 4.5–5.5 hours. Phosphotungstic acid concentration of 13.5%, reaction time of 4.7 hours, and ball milling time of 2.2 hours produced the optimum yield (88.4%). **Figure 7(a)** show the route of the method and **Figure 7(c)** show the short rod-like cellulose nanocrystals obtained with the range of 200–300 nm in length and 25–50 nm in width. The crystallinity index reached 79.6% and the maximum degradation was 348°C.

From those experiments, the use of a ball mill could assist in a shorter reaction time and increased yield. But the crystallinity index would be reduced. Ball mill treatment is known as a process that can decrease the crystalline structure of materials (Feng, Han and Owen, 2004).

### Citric acid

This weak acid that occurs naturally in citrus fruits has the chemical formula  $C_6H_8O_7$ . In biochemistry, it is an intermediate in the citric acid cycle, which occurs in the metabolism of all aerobic organisms. Its melting point at 156°C and its solubility in water could reach 84% w/w at 100°C. The production of citric acid reaches more than two million tons per year to fulfill the raw material of acidifier, flavoring, and chelating agent industries (Apleblat, 2014).

The first use of citric acid to extract nanomaterials is carried out by Yu *et al* (2016). They produced CNC by citric acid/hydrochloric acid mixture and microcrystalline cellulose as the raw material. The resulting CNC has a rod-like shape with the size of 200–250 nm in length and 15–20 nm in width. Yield resulting from this mixture reached 89.5%, highest crystallinity index was 91.4% and maximum thermal degradation was 377.9°C. The same author also used the same raw material and acid mixture with the addition recycle citric acid as the variables. After two recycling processes, the resulting CNC still has a good yield, of which fresh citric acid was 87.8% and 86.5% after the second recycle. The morphological analyses also showed good results, where  $220.8 \pm 26.6$  nm in length and  $13.2 \pm 2.7$  nm in diameter. Thermal degradation after the second process is also not so different which is 347.0°C compare to 357.5°C from its pristine citric acid (Yu *et al.*, 2019).

### Maleic acid

Maleic acid is an organic acid and has chemical formula  $HO_2CCH=CHCO_2H$ . From its structure, maleic acid has dicarboxylic acid structure, a molecule with two carboxyl groups. Maleic acid is an industrial raw material for the production of glyoxylic acid by ozonolysis and an adhesion promoter for different substrates, such as nylon and zinc coated metals. Maleic acid is high soluble in water (78.8 g per 100 ml of water at 25 °C and 392.6 g per 100 ml of water at 97.5°C) (Bährle-Rapp, 2007) and its melting point 130 - 131°C (National Center for Biotechnology Information, 2020).

The first use of maleic acid as a catalyst to hydrolyzed cellulose was made by Mosier *et al* (2001). They used microcrystalline cellulose as a raw material and found that maleic acid could hydrolysis cellobiose with minimal glucose degradation. In 2008, Lu and Mosier (2008) hydrolyzed hemicellulose from corn stover to produced xylose. They found that 0.2 M maleic acid can produce 80–90% xylose yields at reaction temperatures between 100 and 150°C.

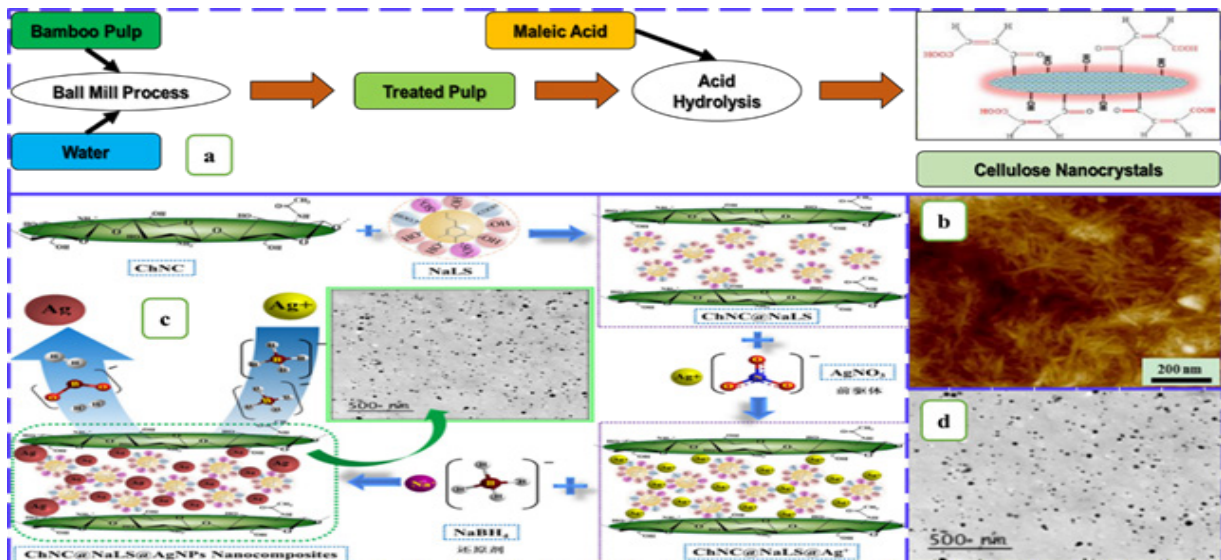
Wang *et al* (2017) used maleic acid to produce CNC and cellulose nanofibers (CNF) from bleached eucalyptus kraft pulp. The mean CNC length was around 450–650 nm and the aspect ratio was 60 and 90. The research group by Bian *et al* (2017a; 2017b) found that the yield of CNC by maleic acid hydrolysis was shown low number (around 6%). The low strength of acid was the reason why they got that result. Instead of the low yield, maleic acid can produce CNC with good characteristics, such as good dispersibility (thanks to two carboxyl groups of maleic acid), can be recycled, and better dimension than CNC made by sulfuric acid hydrolysis (Yeganeh, Behrooz and Rahimi, 2017). Seta's research group tried to overcome the yield problem by combining ball mill method as a pre-treatment before maleic acid hydrolysis as we can see in **Figure 8(a)**. The ball mill treatment can open up the firm structure of bamboo pulp, thus maleic acid molecules are easier to react and extracted more CNC. The yield by this hybrid method could increase 10 times and reduce the length of the CNC as shown in **Figure 8(b)** (Seta *et al.*, 2020). The resulting CNC also showed high colloidal stability after 5 days.

The work to produce ChNC from shrimp shells by maleic acid hydrolysis was worked by Yang's research group, they used hydrolysis temperature of 110°C, 3 hours hydrolysis time, and 80% maleic

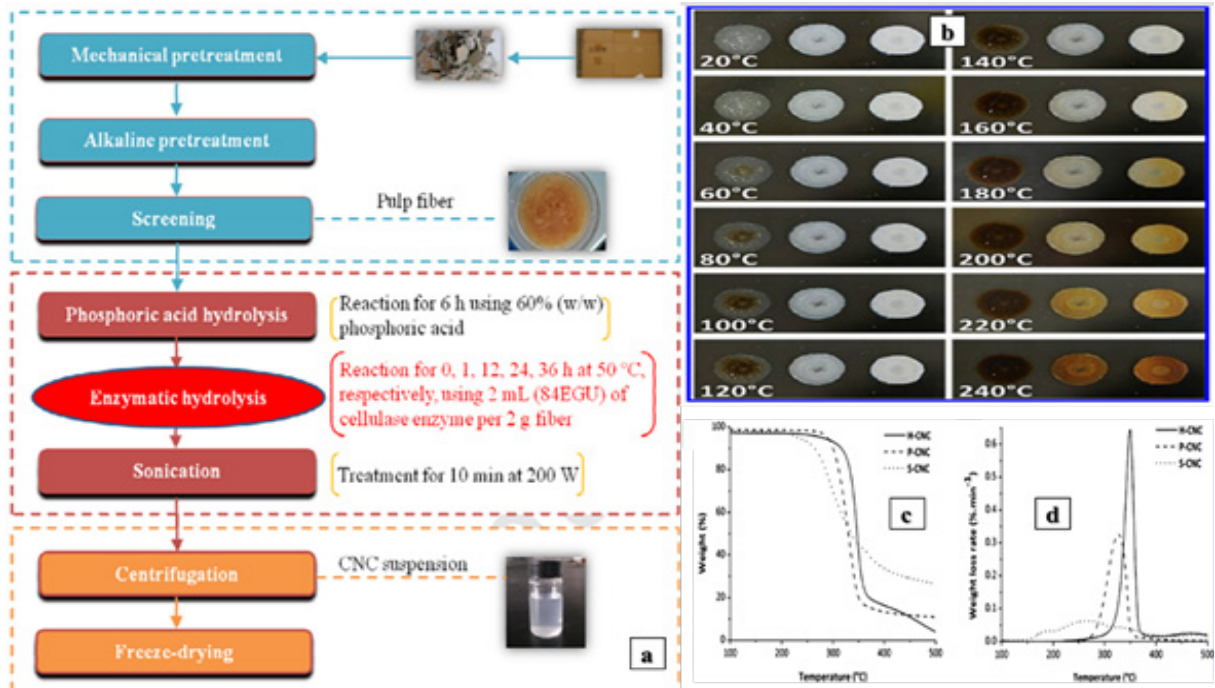
acid. From **Figure 8(c)** and **Figure 8(d)** show the resulted ChNC to collaborate with sodium lignosulfonate and silver nanoparticles to carry out catalytic degradation performance for model contaminants of Congo Red (Yang *et al.*, 2020). The result was very good and this nanohybrid particle can be potentially used in the wastewater field.

### Phosphoric acid

With the chemical formula  $H_3PO_4$ , phosphoric acid is a weak acid and has the appearance of an 85% aqueous solution, which is a colorless, odorless, and non-volatile syrupy liquid. The route to make CNC using phosphoric acid hydrolysis can be seen in **Figure 9**. The first CNC made by phosphoric acid



**Figure 8.** (a) Schematic diagram of ball mill pretreatment and maleic acid hydrolysis (Seta *et al.*, 2020) (b) AFM Image of resulted CNC (Seta *et al.*, 2020) (c) Schematic diagram of ChNC@NaLS@AgNPs nanocomposites (Yang *et al.*, 2020) (d) TEM image of ChNC@NaLS@AgNPs nanocomposites (Yang *et al.*, 2020)



**Figure 9.** (a) Schematic diagram of phosphoric acid CNC made by hybrid method (Tang *et al.*, 2015) (b) Photos of solution-cast samples of S-CNCs (left), P-CNCs (middle), and H-CNCs (right) (Espinosa *et al.*, 2013) (c) TGA traces and (d) derivatives weight loss of CNC made by phosphoric, sulfuric and hydrochloric acid (Espinosa *et al.*, 2013)



hydrolysis was introduced by Lemke *et al* (2012). They used bleached western red cedar kraft pulp as the raw materials to study the phase structure but not the characterization of the CNC.

Espinosa *et al* (2013) use this acid to hydrolyze Whatman no. 1 filter paper and characterized the resulted CNC. They found that the CNC has length of  $316 \pm 127$  nm, diameter of  $31 \pm 14$  nm for the condition of 90 minutes at 100 °C with an  $H_3PO_4$  concentration of 10.7 M. Its crystallinity index reached 81% and the main concern of their research project was the thermal degradation of their CNC were reached 325°C as shown in **Figure 9(c)** and **Figure 9(d)**. The yield reported was 76–80%. They also compared three kinds of CNC (phosphoric, hydrochloric, and sulfuric acid CNC), and they found that CNC made by hydrochloric acid has the best thermal stability among them and CNC made by sulfuric acid was the worst. The results of the thermal stability test of the CNC can be seen in **Figure 9(b)**.

Another work by Tang *et al* (2015) shows in **Figure 9(a)** phosphoric acid can be used as a combined method to produce CNC. They used old corrugated containers (OCC) as their raw materials and combined enzymatic process, phosphoric hydrolysis, and mechanical method (sonication). Enzymatic hydrolysis and mechanical treatment in these works could enhance yield, crystallinity, and thermal stability. The hybrid methods also reduced the length of the resulting CNC. The yield was increased almost 100%, crystallinity was increased from 54.3% to 57.8%, and the thermal stability was increased from 276–312°C.

## Conclusion and Future Perspectives

As renewable and biodegradable biomaterials, chitin and cellulose are taking attraction and will continuously catch interest from both scientists and industry. Recent studies have mainly focused on the preparation of CNC and ChNC by liquid acid hydrolysis and less attention has been paid to the solid acid catalyst, especially for chitin nanoparticles. Solid acid hydrolysis is a promising method to extract CNC and ChNC from its natural resources. Many advantages can result from this method, especially the recycling ability and esterification during the hydrolysis process considering some of these acids have a dicarboxylic group. Many publications have been made for cellulose as the CNC raw materials by solid acid hydrolysis, but very few perspectives regarding chitin nanocrystals. This is an opportunity in the future to explore more about this material. Also,

not so many applications of CNC and ChNC even though it has many positive characteristics. Despite the advantages, the major challenge for the preparation by solid acid hydrolysis is the low yield. To overcome this problem, hydrolysis needs to be combined with other methods, such as mechanical method, enzymatic process, or TEMPO-mediated oxidation process. These hybrid methods can deliver not only efficient preparation of nanocrystals based on targeted cleavage of certain bonds but also can give these polysaccharide-based nanocrystals to be more readily available and be used in broader fields and fulfill industrial feasibility.

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