Isolation, Characterization, and Application of Nanocellulose from Agro-industrial By-products: A Review

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Abstract

Cellulose, consisting of β-anhydro-d-glucose units, is a natural, biodegradable, and versatile biopolymer with several applications in food and non-food systems. Cellulose is probably the most abundant biopolymer in the biosphere and is synthesized by multiple living organisms, ranging from some bacterial species to higher plants. Cellulose recovery was initially done from forest wood mainly. Other sources, including agro-industrial by-products, such as, fruit peels, husks, revealed to be potential reservoirs of cellulose. Recycling agro-industrial waste by recovering cellulose is an ideal strategy to mitigate the impact of food waste from agro-industrial activities. Moreover, the tremendous potential of cellulose nanomaterials has fueled researchers' interest in developing environmentally friendly extraction techniques. The present review paper focuses on the recovery of nanocellulose from different agro-industrial by-products and reports the advantages of the extraction technique used, such as, the use of deep eutectic solvents, ultrasound, steam explosion, mild acids, reduced effluents, amongst others. The importance of characterizing the physico-chemical properties of nanocellulose from different sources is also discussed. It is expected that scientific findings presented in this paper will highlight the potential of agro-industrial wastes as cellulose reservoirs and the importance of physico-chemical characterization of nanocellulose.

Keywords: Nanomaterials; eutectic solvent; crystallinity; purity; thermal degradation

Introduction

Cellulose is considered as the most abundant biopolymer in the biosphere.[1] Although, it can be synthesized by some algae and bacteria, cellulose mainly occurs in plant cells. It was first isolated from plant material by the French chemist Anselme Payen in 1839.[2] Cellulose occurs in plants' cell wall as an amalgam of other biopolymers, namely, pectin, lignin, and hemicellulose, and is referred to as the lignocellulosic biomass.[3] Biopolymer research scientists have delved into the fundamental structure of cellulose from higher plants and discovered that it is made up of millimeter-sized filaments, consisting of continuous microfibers which contain fibrils in the nanometric scale.[4] Cellulose particle in the nanometric scale, referred to as nanocellulose, was reported to possess enhanced characteristics compared with native and micro cellulose. As such, nanocellulose has a large specific surface area, which is estimated to range between tens to hundreds of square meters per gram, and thus enhances interaction with surrounding matrix .[5,6] The mechanical properties of cellulose nanocrystals, including high strength (2–6 GPa), high modulus (130–150 GPa), and low coefficient of thermal expansion (4–6 ppm/K), dictate its structural stabilizing role in Pickering emulsions.[7]

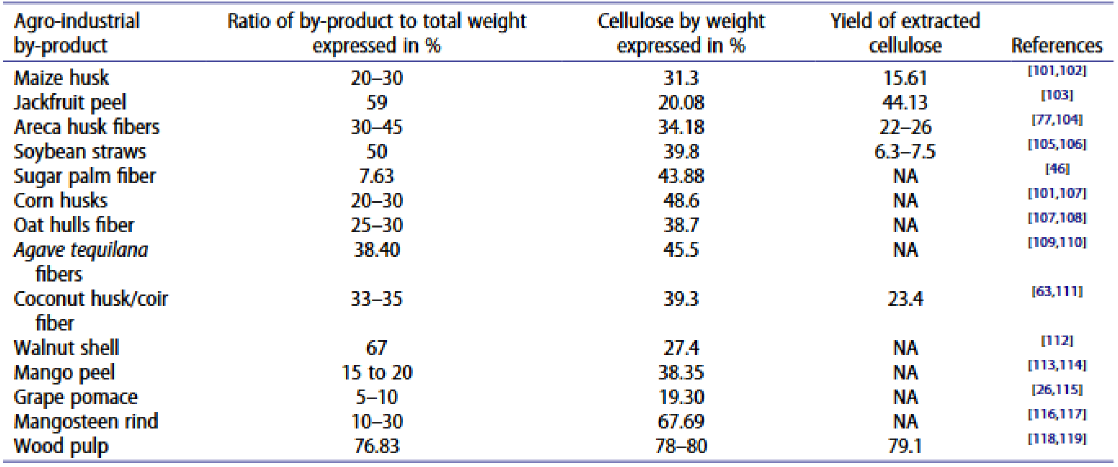
The specificities of nanocellulose which underpin its versatile applications, include abundance, biodegradability, broad compatibility with biological molecules, and ability to modify its structure.[8] Moreover, cellulose nanocrystals and nanofibrils confers exceptional mechanical properties over micro and macro cellulose due to enhance fiber–matrix interface and good dispersion of hydrophilic nanocellulose in matrices[9] . Nanocellulose suspensions are transparent compared to micro and macro cellulose suspensions and this is attributed to smaller and homogeneous fiber size.[10]

The purpose of this review article is to bring forth recent developments about eco-friendly extraction methods of cellulose for agro-industrial by-products and its conversion to the nanometric form. In fact, the numerous attributes of nanocellulose have been the focal point of researchers in academia and industries over the past decades. Besides, the physico-chemical properties of isolated nanocellulose will be presented. Lastly, the potential of nanocellulose in various fields will be analyzed. Data collected will then assist in concluding about studies carried out and potential areas which could be further investigated.

Cellulose in agro-industrial by products

With an annual production of 75 to 100 billion tons, cellulose is among the top most utilized biopolymers .[11] On the other hand, these figures are expected to rise with the concomitant diversification in the use of cellulose derivatives, including nanocellulose. In addition, the debates on the growing concerns with regard to environment preservation and sustainability, have accentuated the pivotal role of valuable compounds recovery from agro-industrial waste. Rice hulls, yerba mate sticks, sugar beet pulp, lime residues, sugarcane bagasse, are examples of agro-industrial wastes (Table 1) that represent low-cost and sustainable sources of nanocellulose.[11] Table 1 shows that wood pulp has the highest content of cellulose as well as the highest yield compared to other sources. Nevertheless, some of the agro-industrial by-products, for example, mangosteen rind, corn husk, have potential for cellulose extraction. It is also noted that the cellulose content and extracted cellulose yield is not available for many fruits and vegetable peels or by-products. Besides, availability of these agro-industrial wastes is supported *via* continuous agro-industrial activities, thereby assuring constant supply. In addition, reusing agro-industrial wastes presents a socially and economically viable strategy to mitigate pollution related to agro-industrial waste disposal.

Table 1. Cellulose content (%) of some agro-industrial by-products.



Agro-industrial by-product	Ratio of by-product to total weight expressed in %	Cellulose by weight expressed in %	Yield of extracted cellulose	References
Maize husk	20–30	31.3	15.61	[101,102]
Jackfruit peel	59	20.08	44.13	[103]
Areca husk fibers	30–45	34.18	22–26	[77,104]
Soybean straws	50	39.8	6.3–7.5	[105,106]
Sugar palm fiber	7.63	43.88	NA	[46]
Corn husks	20–30	48.6	NA	[101,107]
Oat hulls fiber	25–30	38.7	NA	[107,108]
Agave tequilana fibers	38.40	45.5	NA	[109,110]
Coconut husk/coir fiber	33–35	39.3	23.4	[63,111]
Walnut shell	67	27.4	NA	[112]
Mango peel	15 to 20	38.35	NA	[113,114]
Grape pomace	5–10	19.30	NA	[26,115]
Mangosteen rind	10–30	67.69	NA	[116,117]
Wood pulp	76.83	78–80	79.1	[118,119]

*Yield of extracted cellulose: expressed as % of weight of plant material used for extraction; NA: not available.

Structure and chemistry of cellulose and nanocellulose

Cellulose is composed of monomers of glucose units connected by β-d-1,4 glycosidic bond, forming a linear structure which can comprise of 10 000–15 000 units per chain.[12] Monomer units (β-anhydro-d-glucose) consist of three hydroxyl groups linked by hydrogen bonds to adjacent monomers in the same chain or adjacent chain, thereby forming intrachain and intralayer hydrogen bonds.[13] Intramolecular hydrogen bonding occurs between the OH group of C3 hydroxyl group and the adjacent in-ring oxygen while intermolecular hydrogen bond formation involves the OH groups of C2 and C6.[14] These intrachain and intralayer hydrogen bondings stabilize cellulose microfibrils, forming a semi-crystalline structure[15] (Fig. 1). Hydrogen bonds, prominent within the crystalline regions of cellulose fibrils, are related to the toughness, strength, insolubility, fibrousness, and resistance of cellulose to some organic solvents.[13]

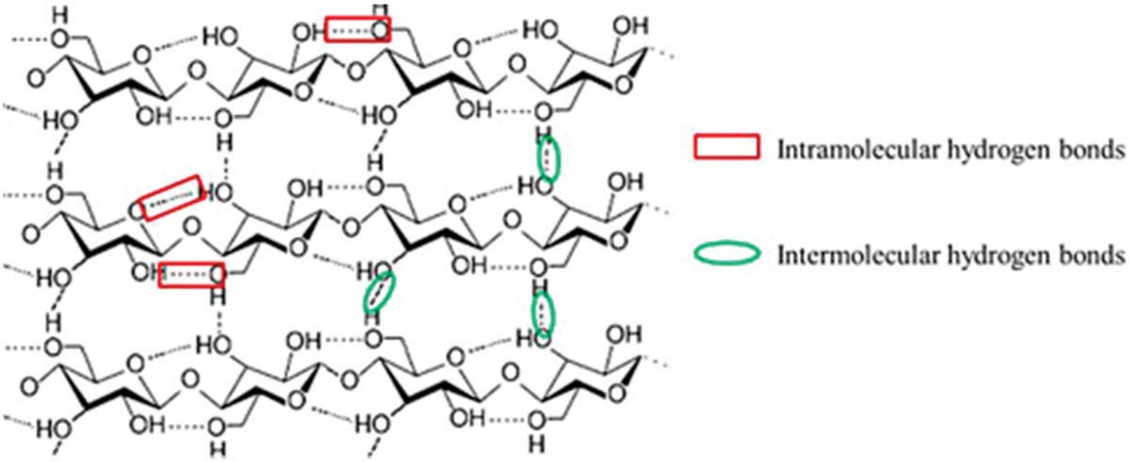


Figure 1. Structure of cellulose[16].

Theoretical and experimental data have confirmed the renewability, sustainability, non-toxicity, and the environmentally friendly use of nanocellulose to address societal and environmental concerns.[3] Cellulose nanostructures, such as, cellulose nanofibrils and cellulose nanocrystals, have gained momentum with the development of nanoscience and nanotechnology. Cellulose nanofibrils or nanofibrillated cellulose or cellulose nanofibers are long, thin, and flexible and consist of alternating crystalline and amorphous regions, whereas cellulose nanocrystals or nanocrystalline cellulose or rod-like cellulose nanocrystals or cellulose nano-whiskers, are obtained after removal of the amorphous regions.[17,18] Table 2 summarizes the different types of nanocellulose and describes the specificity in their structures.

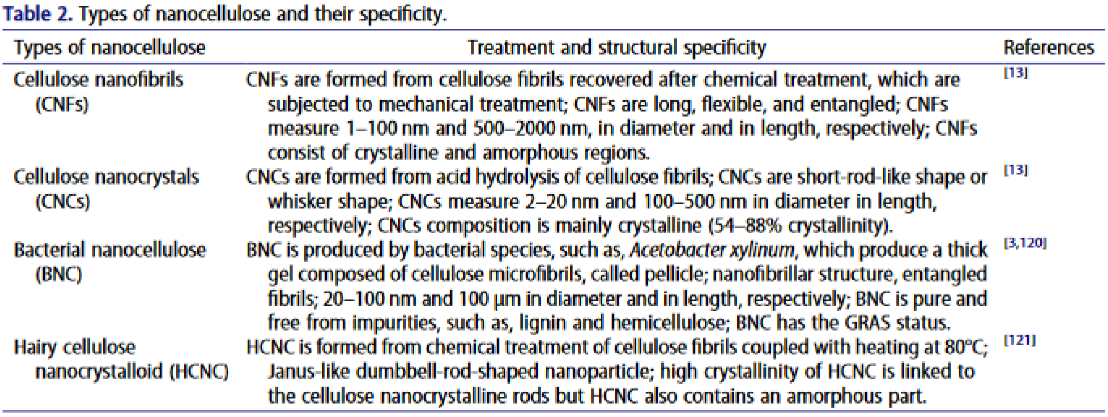


Table 2. Types of nanocellulose and their specificity.

Types of nanocellulose	Treatment and structural specificity	References
Cellulose nanofibrils (CNFs)	CNFs are formed from cellulose fibrils recovered after chemical treatment, which are subjected to mechanical treatment; CNFs are long, flexible, and entangled; CNFs measure 1–100 nm and 500–2000 nm, in diameter and in length, respectively; CNFs consist of crystalline and amorphous regions.	[13]
Cellulose nanocrystals (CNCs)	CNCs are formed from acid hydrolysis of cellulose fibrils; CNCs are short-rod-like shape or whisker shape; CNCs measure 2–20 nm and 100–500 nm in diameter in length, respectively; CNCs composition is mainly crystalline (54–88% crystallinity).	[13]
Bacterial nanocellulose (BNC)	BNC is produced by bacterial species, such as, *Acetobacter xylinum*, which produce a thick gel composed of cellulose microfibrils, called pellicle; nanofibrillar structure, entangled fibrils; 20–100 nm and 100 µm in diameter and in length, respectively; BNC is pure and free from impurities, such as, lignin and hemicellulose; BNC has the GRAS status.	[3,120]
Hairy cellulose nanocrystalloid (HCNC)	HCNC is formed from chemical treatment of cellulose fibrils coupled with heating at 80°C; Janus-like dumbbell-rod-shaped nanoparticle; high crystallinity of HCNC is linked to the cellulose nanocrystalline rods but HCNC also contains an amorphous part.	[121]

Extraction of cellulose

A number of chemical and mechanical treatments are used to extract cellulose and isolate nanocellulose from plant materials and these include, (i) pre-treatment by washing and grinding, (ii) purification by alkali treatment and bleaching, and (iii) hydrolysis of amorphous domains using acid followed by mechanical treatment to obtain the correct nano size.[19] Acid hydrolysis and mechanical treatment are the most currently used methods for nanocellulose recovery at industrial level.[20]

In line with the objective of sustainable development goals, the present century should witness good progress in the development of products derived from biological materials, such as, cellulose, and the advent of green technologies in line with the ecological and sustainable requirements of the society.[21] In this sense, new developments have been made regarding the improvement in the extraction of cellulose. The benefits of novel techniques, such as, high-pressure homogenization, steam explosion, ultrasonication, and enzyme-assisted extraction, in the extraction of cellulose from agro-industrial waste and its conversion to nanocellulose are discussed in the next sections.

Conventional and "non-green chemistry" principles

Fractionation of the lignocellulosic biomass from plant biomaterial is the fundamental principle of cellulose extraction. Successive extraction is used to isolate cellulose from the amalgam of biopolymers. The basic principle includes acid hydrolysis to remove pectin, followed by removal of hemicellulose and lignin (Table 3). It is also important to note that pretreatment, for example, washing with hot water to remove sugars, water-soluble phenolic compounds, and polysaccharides is recommended.[22] This step is often omitted in scientific articles reporting the extraction of cellulose from plant materials (Table 3). Pre-treatment of plant material to remove lipids, waxes, sugars, phenolics, etc., is crucial for the recovery of high purity cellulose.

Table 3. Extraction of cellulose and isolation of nanocellulose using conventional extraction method.

Source	Cellulose extraction	Nanocellulose recovery	Yield (% dry mass) *	Type of nanocellulose	Nanocellulose dimensions	References
Pistachio shells	Lipids were removed from pistachio shell powder using a Soxhlet extractor (ethanol/toluene, at 110°C, overnight). The residue was washed (6 times) with 1 M sodium hydroxide solution for 2 h. The sample was treated with hydrogen peroxide and acetic acid solution (60°C for 2 h). The sample was subjected to Soxhlet extraction to remove excess chemicals and particles.	Acid hydrolysis using sulfuric acid.	50%	Cellulose nanocrystals	Width and length: 12 and 187 nm	[122]
Maize husk	Dried, powdered maize husk was treated at 80°C for 2 h with sodium hydroxide overnight, washed and acidified sodium chlorite, followed by washing until neutral pH was recorded.	Acid hydrolysis using sulfuric acid.	15.61%	Cellulose nanocrystals	Length and width: 940 and 5.84 nm, respectively	[102]
Jackfruit peel	Dewaxed, powdered jackfruit peel was bleached several times using sodium chlorite (pH 3.5, 70°C, 2 h) followed alkaline treatment using sodium hydroxide (60°C for 2 h).	Acid hydrolysis using sulfuric acid.	44.13%	Spherical cellulose nanocrystals	Diameter: 130 nm	[103]
Rose stems	Dried rose stem was treated for 2 h at 80°C with sodium hydroxide, followed by filtration and drying. The residue was treated with hydrogen peroxide and sodium hydroxide for 90 min at 55°C, followed by washing and drying.	Acid hydrolysis using sulfuric acid followed by		homogenization.	17.2%	Cellulose nanofibrils
Diameter: 30 nm	[123]					
Areca husk fibers	Dried, dewaxed material was treated with sodium hydroxide at 50°C for 4 h. Washed residue was treated with hydrochloric acid to separate microfibrils. The material was grinded and treated with alkali and acid. Sodium chlorite and glacial acetic acid (2 h at 60°C) were used to bleach the sample followed by washing	Acid treatment (5 M hydrochloric acid) followed by		homogenization.	22–26%	Cellulose nanofibrils
Diameter: 3–5 nm	[77]					

*The percentage yield was calculated on the dry weight of either crude cellulose or nano material.

In terms of extraction, hot acid treatment, namely, acid hydrolysis ($pH<3$), allows the extraction of acid-soluble polysaccharides and polyphenols.[23] It was noted that most of the cellulose extraction methods did not report pre-treatment in hot acid and this might affect the purity of the cellulose obtained. The plant material is subjected to alkaline treatment for the saponification of intermolecular ester bonds which crosslink xylan hemicelluloses and also lignin.[24] Finally, delignification of the residue is carried out using bleaching chemicals and this generate electrophilic species and in turn attack electron-rich components in aromatic nuclei and unsaturated, ring conjugated side chains.[25] Hydrogen peroxide, a bleaching agent currently used in cellulose extraction, oxidizes and dissolves residual lignin and phenolics and yield white crude cellulose.[26] Sodium chlorite, used in the chemical treatment of plant material for the extraction of cellulose, is highly reactive and highly corrosive and requires careful handling to avoid damage to pipe work and equipment.[27] Sodium chlorite can generate absorbable organic halides and effluents can increase soil and water toxicity.[28] Moreover, the recovery of nanocellulose requires the use of strong acid-based hydrolysis alone or in combination with mechanical treatment, such as, homogenization. Conventional extraction is lengthy and involves a lot of energy to produce nanocellulose in the crystal and fibril form. These harsh chemicals used for cellulose extraction are not considered as "green" or as environment friendly.

Enzymes

Biological methods can minimize impact on the environment and therefore fall under the eco-friendly category. Hemicellulases, including, xylanase and β-glucanase, act on non-starch polysaccharides composed of xylan, xylobiosa, arabinoxylans, and arabinogalactan, and thus help in disrupting the integrity of the cell wall.[29] On the other hand, polygalacturonase, a cell-wall degrading enzyme, hydrolyses α 1–4 bonds of the pectin backbone. Cellulases, such as, endoglucanases, act on amorphous portions of the cellulose structure, breaking the polymer into smaller structures, thereby producing cellulose nanocrystals .[30] The use of enzymatic treatment in the recovery of nanocellulose includes a number of advantages, namely, the partial or total elimination of chemicals; control of enzyme dosage, operational conditions and enzymes cocktail composition enhance specificity of final material and high process control .[31]

Enzyme treatments are often employed alongside chemical pre-treatment, as efficiency of the enzyme treatments can be limited due to the encapsulation of cellulose by other components, such as, pectin, hemicellulose, and lignin.[32] However, a study by Bauli et al.[33] demonstrated that it was possible to recover cellulose nanocrystals from wood flour without chemical pre-treatment (Table 4). A recent investigation conducted by Perzon et al.[34] also reported a one-pot procedure to produce cellulose nanofibrils from sugar beet pulp using enzymes. Exclusion of the chemical pre-treatment which requires multiple washing steps lowered the water consumption by 67%. Scientific studies investigating the recovery of nanocellulose from agro-industrial by-products without chemical pre-treatment are limited. Chemical pre-treatment produces toxic effluents which is not in line with environmentally friendly concepts. Another limitation to the use of enzyme might be related to the constraints of maintaining optimal temperature and pH conditions. In addition, while processing agro-industrial waste, there is a possibility of interference by compounds, such as, secondary metabolites for example flavonoids, phenolic compounds, which might affect enzymes effectiveness .[35]

Table 4. Extraction of cellulose and isolation of nanocellulose using enzymes.

Source	Cellulose extraction	Nanocellulose recovery	Yield (% dry mass)*	Type of nanocellulose	Nanocellulose dimensions	References
Sugar beet pulp	A cocktail of enzymes (β-glucanase, polygalacturonase, endo-xylanase, cellulase, α-amylase) 40°C for 2 h at pH 9. Enzymatic action was stopped by adding 1% sodium chlorite and heating to 70°C for 2 h. The sample was washed until no oxidation was observed.	High-shear homogenization.	NS	Cellulose nanofibrils	Length and diameter: ≥ 1 µm and 5–40 nm, respectively	[34]
Wood flour	No crude cellulose extraction was performed.	Wood flour was milled (297 µm) and subjected to enzyme cocktail (endoglucanase and xylanase) for 48 h in a buffered citrate solution of 1.5% sodium citrate and 0.5% citric acid at 50°C.	2.83%	Cellulose	nanocrystals	Width and length: 66.4 and 162 nm,
respectively	[33]					
Sugar beet pulp	Viscozyme L (10 µL/g pulp) (main active enzyme β-glucanase (endo1,3(4)-)), Pectinex Ultra Clear (10 µL/g pulp) (main active enzyme polygalacturonase), Pulpzyme HC (10 µL/g pulp) (main active enzyme endo-xylanase (endo1,4-)), and Aquazyme 240 L (10 µL/g pulp) (main active enzyme α-amylase) for 24 h at 40°C and pH 4 (0.1 M sodium acetate buffer).	High-shear homogenization at 500 bars for 18 min.	NS	Cellulose nanofibrils	Width: 5–130 nm	[32]
Potato pulp	Viscozyme L (15 µL/g pulp) (main active enzyme β-glucanase (endo1,3(4)-)), Pectinex Ultra Clear (15 µL/g pulp) (main active enzyme polygalacturonase), and Aquazym 240 L (5 µL/g pulp) (main active enzyme **α**-amylase) for 24 h at 40°C and pH 4 (0.1 M sodium acetate buffer).	High-shear homogenization at 500 bars for 18 min.	NS	Cellulose nanofibrils	Width: 5–130 nm	[32]
Soybean straws	Sodium hydroxide (90°C for 1 h repeated twice, or 30°C for 15 h). Washed material was bleached (0.7% acetic acid and 3.3% sodium chlorite, agitated at 75°C for 4 h; and hydrogen peroxide, sodium hydroxide 2%, and magnesium sulfate 0.3% at 90°C for 3 h).	Subjected to enzymatic cocktail (endoglucanase, xylanase, β-glucosidase, exoglycosidase, and filter paperase) at 50°C, pH 4.0, for 42 h.	6.3–7.5%	Cellulose nanofibrils	Diameter and length: 15 and, 300 nm, respectively	[106]

*The percentage yield was calculated on the dry weight of either crude cellulose or nano material. NS: not specified.

The high price and limited commercial availability of most enzymes is another major problem .[36] Companies like Novozymes have devoted themselves to the development of new cellulases using genetic engineering with added benefits, including the economical production of cellulases by process and strain enhancement and improvement in the specificity of cellulases .[36] For instance, in order to remove amorphous regions of cellulose fibers to produce nanocellulose, a cocktail of Cellic®CTec2, containing cellulases, β-glucosidase, hemicellulase, and Cellic®HTec2, an endoxylanase was used.[37] However, conversion yields are usually low (Table 4). Achieving higher yields requires chemical pretreatments of the heterogeneous biomass to produce cellulose rich material as well as untangling the densely packed cellulose, making the cellulose molecule more accessible to enzymatic hydrolysis .[38]

A two-step process comprising of ethanol and peroxide solvothermal pretreatment and ultrasonication to isolate cellulose nanocrystals from wood flour, and reported a yield of 44.14% .[39] The morphology of the nanocellulose depends on the specificity of the enzymes. As such, endoglucanases attack amorphous regions of cellulose and is used in the production of cellulose nanocrystals.[40] Rod-like and spherical cellulose nanocrystals were obtained from bleached Kraft eucalyptus pulp treated with an enzyme cocktail composed of cellulase and xylanases .[41] This method allowed the fine-tuning of the cellulose nanocrystals morphology because of the specificity of the enzymes used. Xylanases promote the accessibility the fibers while cellulases at high concentration aggressively attack the cellulose molecule producing spherical cellulose nanocrystals, thereby highlighting the importance of controlling the cellulase to xylanase ratio.[42]

High pressurized homogenization

The application of the concept of high pressurized homogenization in the recovery of cellulose nanofibrils was first reported in 1983.[16] The word “homogenization” refers to the capacity of producing a homogenous suspension consisting of homogenous particles, i.e., particle of regular size, by applying pressure to force the mixture through a specifically designed orifice having a diameter in micrometer range (Fig. 2) .[44] This mechanical process has been found to promote fibrillation of cellulose fiber, resulting in the formation of a homogeneous suspension with many individual nanostructures.[45] High pressurized homogenization is regarded as an eco-friendly method due to its efficiency, simplicity, and organic-free procedure.[46] High pressurize homogenization is mostly used as a pre-treatment of the crude cellulose for nanocellulose recovery (Table 5). In brief, the cellulose slurry is passed through a very small nozzle (50–200 µm) under high pressure to mechanically isolate cellulose nanofibrils from microfibers and homogenization is favored by cavitation as well as high shear .[46] The numerous intermolecular and intramolecular hydrogen bonds existing within the cellulose network, are responsible for its insoluble nature in water and most organic solvent, and this might cause clogging of the homogenizer nozzle.[47] In order to prevent clogging, maximum reduction the particle size is necessary and this is achieved through pre-treatments. For example, for the recovery of cellulose nanofibrils from sugar palm fiber, the crude cellulose was refined in a milling machine (20 000 revolutions), in order improve fibers accessibility, fibrillations, and fluidity.[46] Inclusion of pre-treatment steps, such as, steam explosion, ball milling, microfluidizer processor, alongside high-pressure homogenization technology increase the capital investment and training cost.

Table 5. Isolation of nanocellulose after cellulose extraction using high pressurized homogenization.

Source	Cellulose extraction	Nanocellulose recovery	Yield (% dry mass) *	Type of nanocellulose	Nanocellulose dimensions	References
Sugar palm fiber	Delignification and mercerization following standard ASTM D1104-56 and ASTM D1103-60, respectively produced crude cellulose which was milled (ISO 5264–2:2002).	High pressurized homogenization (500 bars)	92%	Cellulose nanofibrils	Diameter: 5.5 nm	[46]
Corn husks	The sample was treated with 0.1 M sodium hydroxide for 18 h at 30°C, then 0.1 M nitric acid for 1 h at 85°C and finally with 3% hydrogen peroxide (70°C, 1 h). The sample was treated at room temperature with TEMPO, sodium bromide, sodium chlorite under gentle agitation, pH 10.5. The reaction was stopped when stable pH was reached.	High pressure homogenization (600 bars).	NS	Cellulose nanofibrils	Width: <20 nm	[107]
Oat hulls fiber	The sample was treated with 0.1 M sodium hydroxide for 18 h at 30°C, then 0.1 M nitric acid for 1 h at 85°C and finally with 3% hydrogen peroxide (70°C, 1 h). The sample was treated at room temperature with TEMPO, sodium bromide, sodium chlorite under gentle agitation, pH 10.5. The reaction was stopped when stable pH was reached.	High pressure homogenization (600 bars).	NS	Cellulose nanofibrils	Width: <20 nm	[107]
Lime residues	Lime residues consisting of the flavedo, albedo, segments and juice sacs, were blended (particle size 1–3 mm), autoclaved at 120°C for 2 h, and filtered.	High shear homogenizer (20,000 rpm for 15 min) and high pressure homogenizer (40 MPa) 5 times.	31.01%	Cellulose nanofibrils	Diameter: 3–10 nm	[53]
Soy pulp	Material was treated with choline chloride–oxalic acid type solvent (100°C, 30–120 min, 40 RPM). Distilled water was used as a reverse phase solvent to precipitate cellulose. Solid substrate was washed by distilled water until neutral pH.	High pressure homogenization (60 MPa)	42.13%	Cellulose nanofibrils	Diameter: 27 nm % cellulose: 92.6%	[48]

*The percentage yield was calculated on the dry weight of either crude cellulose or nano material. NS: not specified.

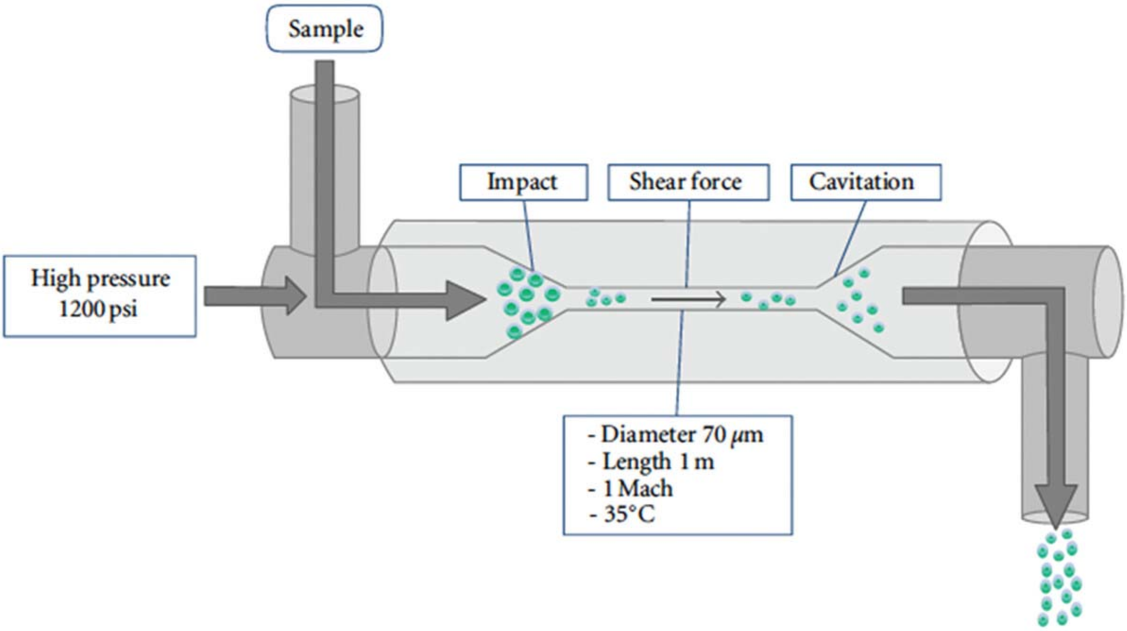


Figure 2. Schematic representation of high pressure homogenization[43].

High-pressure homogenization is often associated to harsh chemical pre-treatments to isolate crude cellulose from biomass (Table 5). Green solvents might be an alternative to these harsh chemicals. The recovery of cellulose nanofibrils from okara or soy pulp was possible using high-pressure homogenization coupled with deep eutectic solvents treatment.[48] Deep eutectic solvents, exhibiting good solvent capacity and negligible vapor pressure reducing volatile organic compound emissions, are promising green solvents which can be produced from inexpensive, biodegradable, and recyclable ingredients.[49] Deep eutectic solvents are generally produced by the complexation of a hydrogen bond acceptor (halide salts of quaternary ammonium) and a hydrogen bond donor (urea, glycerol).[50] Hydrogen-bonding basicity of deep eutectic solvents favors the dissociation of hydrogen bonds in cellulose macromolecule, thereby enhancing cellulose solubility.[51] Deep eutectic solvents are also used to convert cellulose to the nanometric form. The strong hydrogen bonds of the cellulose molecules (Fig. 3) may be weakened as a result of competing hydrogen bond formation between the ions present in the deep eutectic solvent and the hydroxyl groups of the carbohydrate, consequently provoking the hydrolysis of intramolecular hydrogen bond network.[52] High-pressure homogenization was employed in another study conducted by Jongaroontaprangsee et al.[53] aiming at recovery of nanocellulose from lime residues. Interestingly, the process used was chemical-free, with no alkaline and/or acid pre-treatments. Hydrothermal treatment by autoclaving might have caused the autohydrolysis of hemicellulose, hydrolyzing acetyl groups attached to xylan backbone to acetic acid.[53] However, autoclaving alone had no effect on lignin, except when combined with alkaline reagents.[54] Yield of nanocellulose was higher compared to enzymatic treatment (Table 4). High-pressure homogenization applies mechanical force to convert cellulose to the nanometric form without specifically targeting the amorphous region and thus mostly produce cellulose nanofibrils.

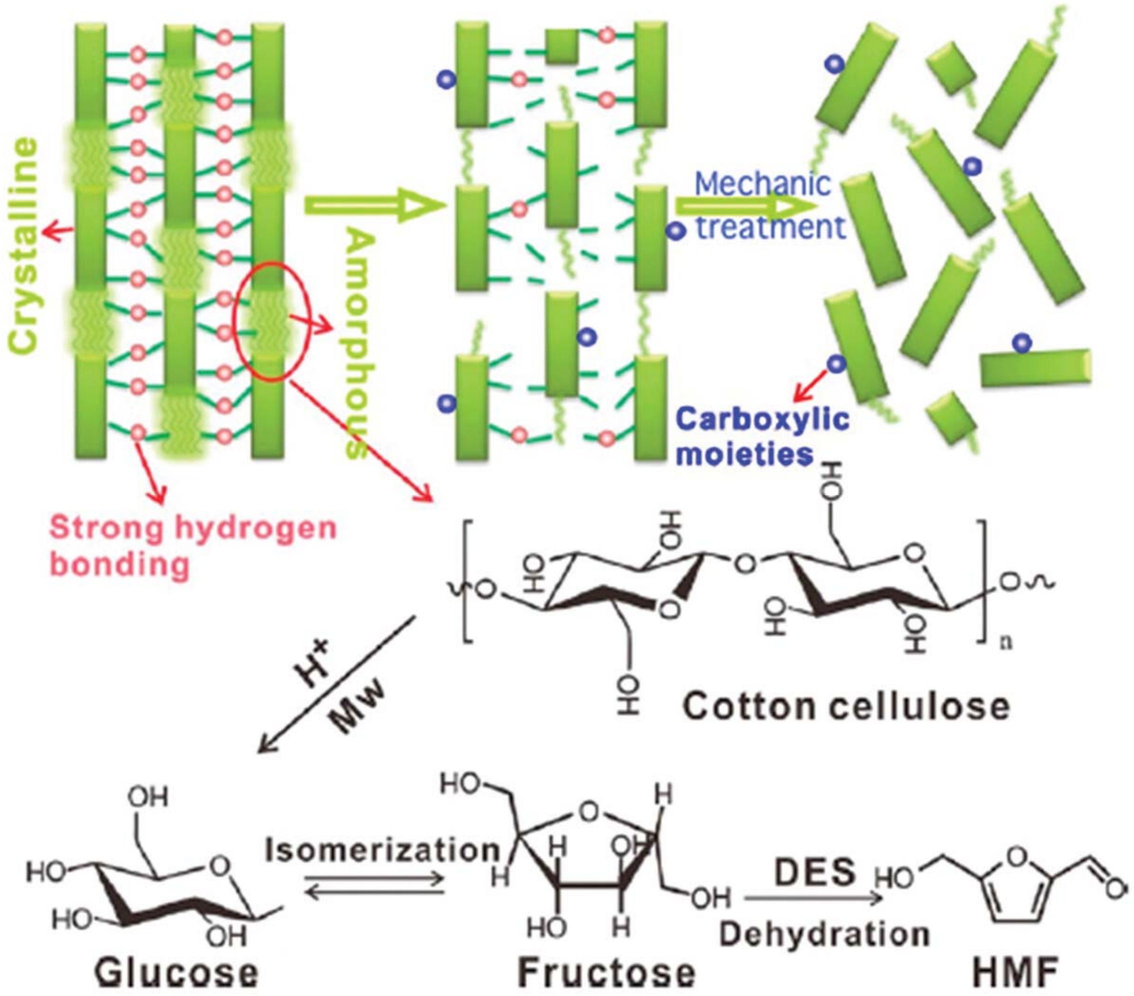


Figure 3. Schematic representation of cellulose recovery using deep eutectic solvent (DES) pretreatment, followed by mechanical treatment[52].

Ultrasonication

The use of ultrasound technology has gained increased interest over the past decades, especially in the isolation of biopolymer. Among the different mechanical techniques used for the recovery of nanocellulose, ultrasonication is one of the most popular method .[55] The principle behind this emerging method has been extensively described in literature. In a nutshell, pressure fluctuations caused by ultrasonic waves (20–100 kHz) form microbubbles that collapse, forming microjets that disrupt cellular structures.[56] Ultrasonication is employed in the last step of nanocellulose recovery and is often conducted following an acid treatment (Fig. 4). Strong acid treatment carried out under strictly controlled conditions of time, temperature, and agitation, promotes hydrolysis of transversal amorphous portions of cellulose microfibrils, thereby yielding highly crystalline (54% to 88%) cellulose rod-like structures.[58] Several factors, including, low energy requirement, short treatment time, reduced solvent use, and improved yield, contribute to the classification of ultrasonication under the umbrella of green technologies. While the technology exhibits great promise as a green method, its use alongside acid hydrolysis in the recovery of nanocellulose defeats the purpose. Moreover, aging of the instrument, decrease ultrasound intensity, thus reducing the reproducibility.

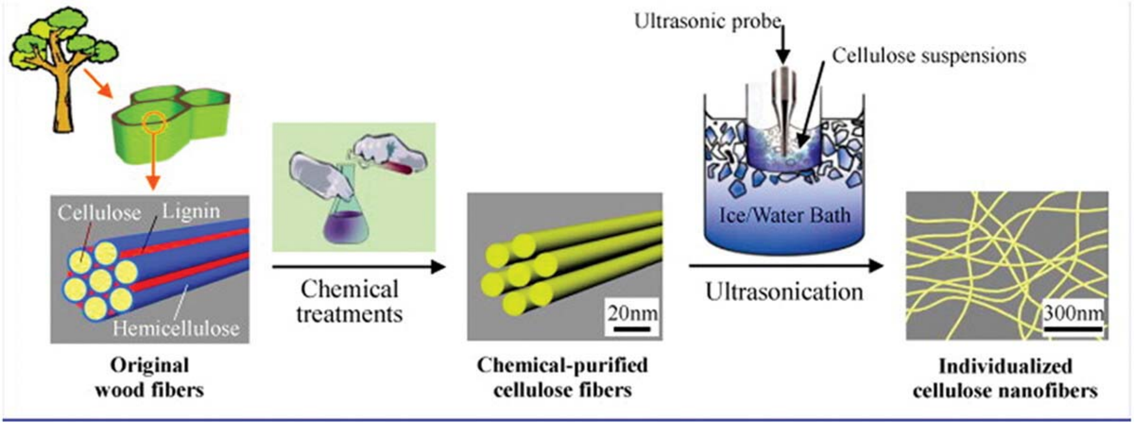


Figure 4. Schematic representation of the application of ultrasound treatment in the isolation of nanocellulose[57].

Chen and co-workers[57] evaluated the effect of different ultrasonic treatment output power on the production of cellulose nanofibrils from chemically pre-treated crude cellulose isolated from wood powder obtained from poplar trees. At 400 W, large aggregates consisting of wire-like cellulose fibers were observed (Fig. 5); at 800 W, greater than 75% of the cellulose nanofibrils had diameter ranging from 5 to 20 nm with a large number of individualized cellulose nanofibrils; at 1000 W and 1200 W, cellulose nanofibrils had uniform width ranging from 5 to 20 nm with an average diameter of approximately 13 nm, forming a web-like structure.[57] The absence of acid hydrolysis step might be strongly related to the absence of cellulose nanocrystals since acid hydrolyses the amorphous region. Ultrasonication was employed during the different steps of crude cellulose extraction and cellulose nanofibril recovery from Fique tow (Table 6). This might be presented as a good strategy, since the heating step, involving a lot of energy is replaced. Moreover, the treatment time can be substantially reduced.

Table 6. Isolation of nanocellulose using ultrasonication.

Source	Cellulose extraction	Nanocellulose recovery	Yield (% dry mass) *	Type of nanocellulose	Nanocellulose dimensions	References
Agave tequilana fibers	The sample was treated a solution of acetic acid, sodium chlorite and sodium hydroxide at 70°C for 1.5 h. Residue was washed and dried at 105°C. Sample was bleached in a solution of sodium hydroxide for 30 min. Cellulose obtained was washed with a solution of sodium hydroxide and acetic acid. The residue was washed with distilled water until neutral pH and dried at 100°C.	Sample was treated with sulphuric acid at 50°C, 1 h, under mechanical stirring, then homogenized and subjected to ultrasonic treatment.	NS	Cellulose nanocrystals	Diameter and length: 11 and 323 nm, respectively	[110]
Barley husks	The ground material was treated with a solution of acetic acid, sodium chlorite and sodium hydroxide at 70°C for 1.5 h. Residue was washed and dried at 105°C. Sample was bleached in a solution of sodium hydroxide for 30 min. Cellulose obtained was washed with a solution of sodium hydroxide and acetic acid. The residue was washed with distilled water until neutral pH and dried at 100°C.	Sample was treated with sulphuric acid at 50°C, 1 h, under mechanical stirring, then homogenized and subjected to ultrasonic treatment.	NS	Cellulose nanocrystals	Diameter and length: 10 and 329 nm, respectively	[110]
Sugarcane bagasse	Bagasse powder was mixed nitric acid for 2 h at 80°C, then washed. The sample was treated with 1% sodium hydroxide at constant stirring for 2 h at 80°C, then washed and bleached with 0.735% sodium hypochlorite. Residue was subjected to acetic acid for 2 h at 80°C, then washed and left to dry.	Crude cellulose was treated with sulfuric acid at room temperature for 24 h, washed, and dialysed with deionized water several times and ultrasonicated.	NS	Cellulose nanocrystals	Particle size: 38 nm	[124]
Rice straw	Rice straws were soaked in hot water for 1 h to remove wax and other substances, then dried in an oven (40°C) overnight. The rice straws were grinded and treated with sodium hydroxide(121°C, 1 h). The washed, dried residues were treated with acidified sodium chlorite (75°C, 90 min).	The sample was washed and treated with sulphuric acid, re-washed and ultrasonicated.	90.28%	Cellulose nanocrystals	Diameter: 5–15 nm	[125]
Fique tow	Fique tow was washed and sonicated in water for 1 h at 40°C to remove remaining juice, water soluble materials. Cut tow was sonicated in hydrogen peroxide adjusted to pH 11.5 with sodium hydroxide (70°C, 120 min). The material washed and dried, was treated with TEMPO, sodium bromide, and sodium chlorite in a sonication bath.	The neutralized material was ultrasonicated.	NS	Cellulose nanofibrils	Diameter: 100 nm	[68]

Table 6. (Continued).

Source	Cellulose extraction	Nanocellulose recovery	Yield (% dry mass) *	Type of nanocellulose	Nanocellulose dimensions	References
Borassus flabellifer leaf stalk residues	Pulverised material was treated twice with sodium hydroxide (120°C, 1 h), followed by washing. Dried residue was treated with acetate buffer and sodium hypochlorite (90°C, 2 h).	Washed, dried residue was treated with sulphuric acid at 45°C for 15 min, followed by washing and ultrasonication (20 kHz, 750 W for 15 min).	NS	Cellulose nanofibrils	Diameter and length: 2 − 27 nm and 0.5 − 1 µm, respectively	[126]
Oil palm empty fruit bunch chlorine free pulps	NS	Sulphuric acid hydrolysis, followed by ultrasonication.	NS	Cellulose nanocrystals	Diameter and length: <20 nm and >100 nm, respectively	[127]
Garlic straw	Dried, powdered garlic straw was treated with sodium hydroxide for 12 h, followed by heating (80°C) in chlorite solution for 2 h.	Treated with sulphuric acid (45°C, 40 min). The washed material was ultrasonicated.	19.6%	Cellulose nanocrystals	Diameter and length: 6 and 480 nm, respectively	[128]
Mengkuang leaves	Trimmed, washed, boiled, dried, grinded leaves were treated with sodium hydroxide (125°C, 2 h), sodium chlorite (125°C, 2 h).	The washed residue was treated with sulphuric acid at 45°C for at 45 min, washed and ultrasonicated.	45%	Cellulose nanocrystals	Diameter and length: 5–25 and 50–400 nm, respectively	[129]
Banana rachis	Degreased and degummed, powdered material was treated with sodium hydroxide for 7 h at 25°C, washed, and dried overnight. The residue was treated acetic and nitric acid 110°C for 20 min. The material was washed and dried at 55°C for 12 h	Acid hydrolysis using sulfuric acid followed by ultrasonication.	23.6%	Cellulose nanocrystals	91 to 102 nm	[130]

The percentage yield was calculated on the dry weight of either crude cellulose or nano material. NS: not specified.

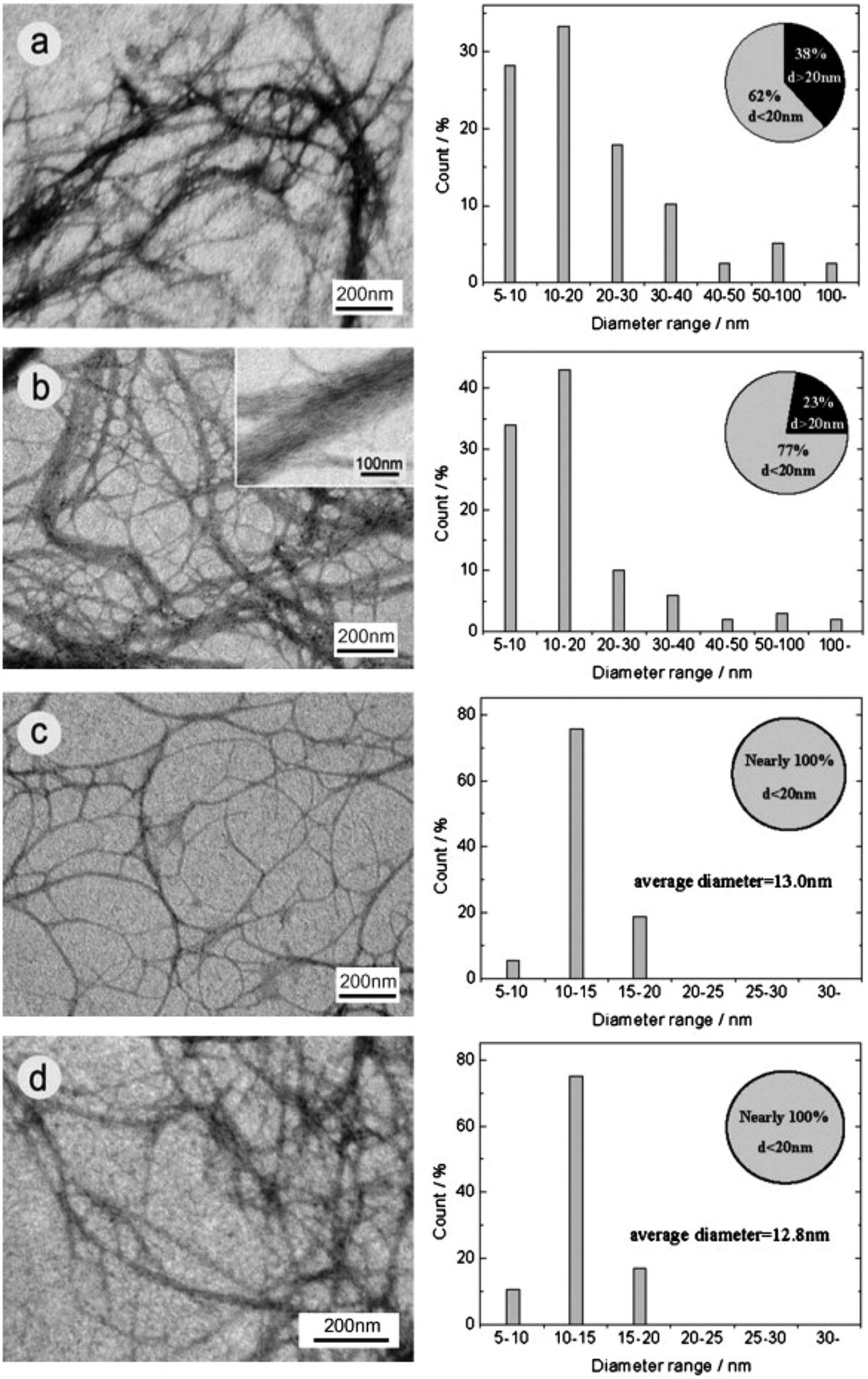


Figure 5. Micrographs of the transmission electron microscopy of cellulose nanofibrils and diameter distribution after ultrasonic treatment at 400 W (a), 800 W (b), 1000 W (c), and 1200 W (d)[57].

Steam explosion

During steam explosion, the plant material is subjected to high temperature (160–260°C) and high pressure (7–50 bar) for a short period of time (30 s–20 min) in a closed vessel, followed by a sudden release of pressure which cause an explosive effect on the cells.[59] The flash evaporation of water caused by the sudden release of pressure exerts thermo-mechanical force on the cells, causing rupture of the cell components.[54] Steam explosion causes the hydrolysis of glycosidic bonds in hemicelluloses and the cleavage of hemicellulose-lignin bonds, resulting in an increased water solubilization of hemicelluloses and in an increased solubility of lignin in alkaline or organic solvents .[60] Apart from reducing non-cellulosic fraction of treated biomass, steam explosion also cause fibrillation, liberating agglomerated fibers into individual entities.[54] In some studies fibrillation is further promoted by the use of chemicals, such as, sodium hydroxide .[61]

The use of steam explosion pre-treatment in the extraction of cellulose encompasses several advantages, namely, low capital investment, low-energy requirements, and low environmental impact.[62] A study carried out by Abraham and colleagues[63] aimed at developing an environmentally friendly approach for the recovery of cellulose nanofibrils from coir fiber. The hot alkaline treatment step was shorter while using steam explosion. Mild acid treatment using oxalic acid, an organic acid, followed by steam explosion and ultrasonication was carried out to isolate the nano material. Nanocellulose obtained by steam explosion is mostly in the fibril form (Table 7). One major limitation associated to use of steam explosion in the recovery of nanocellulose is the lack of selectivity, i.e., recovery of cellulose nanocrystals or nanofibers. Besides, there is a limited number of scientific studies reporting the use of green solvents alongside steam explosion for the recovery of nanocellulose.

Other novel extraction methods

Supercritical fluid extraction, particularly supercritical carbon dioxide assisted extraction, has been extensively used for the recovery of several types of natural compounds. However, studies reporting the use of supercritical carbon dioxide assisted extraction of recovery cellulose from agro-industrial are limited. Albarelli and colleagues[64] reported the production of nanocellulose from sugarcane bagasse using supercritical carbon dioxide assisted extraction coupled with steam explosion or organosolv as pre-treatments, followed by enzymatic hydrolysis. The economic, environmental, and energetic appraisal of the different techniques was conducted. In terms of nanocellulose production, pretreatment involving supercritical carbon dioxide assisted extraction coupled with steam explosion, followed by enzymatic hydrolysis showed promising economic, environmental, and energy benefits. Supercritical carbon dioxide assisted extraction has also been reported in the extraction of cellulose from cassava pulp waste. Cassava pulp waste was treated for 60 min and 120 min at variable temperature (40°C to 80°C) and pressure (8 MPa to 20 MPa). Following supercritical carbon dioxide treatment, surface area of extracted cellulose was enhanced by 16%, due to better dissociation of the cellulose fibrils. Increasing pressure, improved thermal stability. An increase in crystallinity (5%) was observed when extending the treatment time from 60 to 120 min (20 MPa, 60°C).[65] Kenaf fibers, bleached using a chlorine free treatment, were subjected to supercritical carbon dioxide assisted extraction (50 MPa, 60°C, 2 hr), followed by mild acid hydrolysis to produce cellulose nanofibers. Recovered cellulose nanofibers had diameter ranging from 10 to 15 nm and a crystallinity index of 92.8%.[66] Cold plasma assisted extraction is considered as an emerging green technology for the recovery of natural compounds. As far as our literature search could ascertain, there is a dearth of scientific studies

Table 7. Extraction of cellulose and isolation of nanocellulose using steam explosion.

Source	Cellulose extraction	Nanocellulose recovery	Yield (% dry mass) *	Type of nanocellulose	Nanocellulose dimensions	References
Coconut husk/ coir fiber	Coconut husk was treated with 2% caustic soda for 6 h at 25°C. Steam explosion was carried out using a laboratory autoclave (137 Pa, 1 h, 100–150°C). Bleaching with sodium chlorite (pH 2.3, 1 h, 50°C).	Mild acid treatment (5% oxalic acid) followed by steam explosion. Washed fibers were subjected to mechanical stirring and ultrasonication.	23.4%	Cellulose nanofibrils	Diameter: 5–10 nm	[63]
Pineapple leaf fibers	Fibers were treated with 2% sodium hydroxide in an autoclave for 1 h at 20 lb. Steam exploded fibers were washed to neutral pH and bleached six times using a sodium hydroxide, acetic acid, and sodium hypochlorite.	Bleached fibers were washed and dried and treated with oxalic acid (20 lb for 15 min) under steam explosion conditions. The process was repeated 8 times. The material was subjected to mechanical stirring.	NS	Cellulose nanofibrils	Diameter: 5–60 nm	[54]
Wheat straw fibers	The fibers were soaked in sodium hydroxide solution (2%) overnight and treated in a 10–12% solution in an autoclave (15 lb, 4 h). After release of pressure, the process was repeated. The residue was washed several times, soaked in hydrogen peroxide solution (8%) overnight and washed.	The residue was ultrasonicated (60°C, 5 h) with hydrochloric acid (10%) and washed. The material was stirred using a high shear homogenizer (15 min).	NS	Cellulose nanofibrils	Diameter: 30–50 nm	[131]
Yerba mate residues	Steam explosion was carried out using an autoclave (127°C, 1.5 bar, 1 h, 3 times). Washed samples were bleached (10% hydrogen peroxide (w/v), 50°C, 2 h). pH was adjusted neutral and acid treatment combined with steam explosion (5% (w/v) oxalic acid, 127°C, 1.5 bar, 1 h) was performed 3 time. pH of sample was adjusted to neutral.	Homogenized (26,000 rpm for 5 min).	NS	Cellulose nanofibrils	Length and diameter: 279 and 11.4 nm, respectively	[11]

The percentage yield was calculated on the dry weight of either crude cellulose or nano material. NS: not specified.

reporting the use of cold plasma assisted extraction for the extraction of cellulose from agro-industrial by-products for the production of nanocellulose.

Characterization of nanocellulose

A comprehensive understanding of the structure and properties of nanocellulose is of great importance while considering prospective applications. As such, main structural characteristics including, size, shape, crystallinity, purity, and degree of polymerization should be determined.

Crystallinity of nanocellulose

The ratio of crystalline to amorphous domains or the percentage crystallinity of nanocellulose is an important criterion which determines physico-chemical and functional properties. Crystallinity index (%) of cellulose has been used to interpret the changes in cellulose molecular structure following chemical, mechanical, and enzymatic treatments. ^{13}C nuclear magnetic resonance (NMR) spectroscopy, IR spectroscopy, X-ray diffraction (XRD) are the different techniques used to assess crystallinity index, and XRD is the most currently used method. The basic principle and limitations of XRD, IR, and NMR in the determination of nanocellulose crystallinity are shown in Table 8.

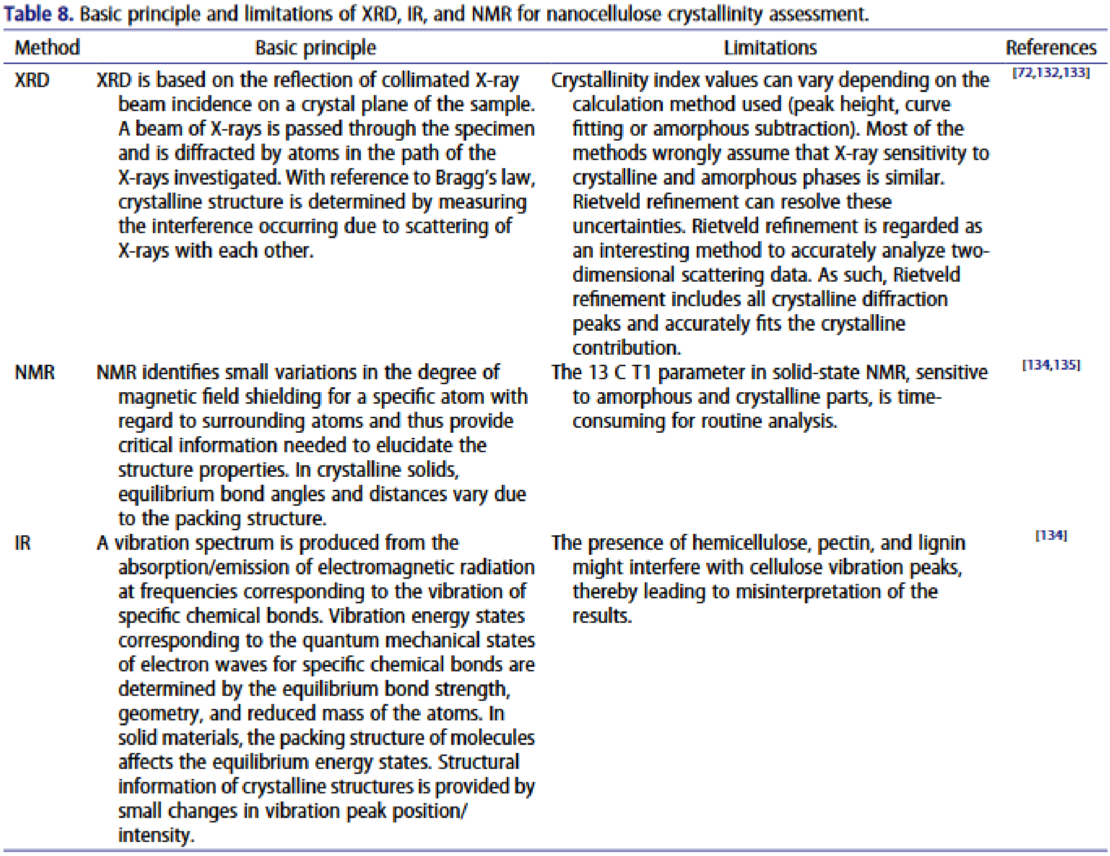


Table 8. Basic principle and limitations of XRD, IR, and NMR for nanocellulose crystallinity assessment.

Method	Basic principle	Limitations	References
XRD	XRD is based on the reflection of collimated X-ray beam incidence on a crystal plane of the sample. A beam of X-rays is passed through the specimen and is diffracted by atoms in the path of the X-rays investigated. With reference to Bragg's law, crystalline structure is determined by measuring the interference occurring due to scattering of X-rays with each other.	Crystallinity index values can vary depending on the calculation method used (peak height, curve fitting or amorphous subtraction). Most of the methods wrongly assume that X-ray sensitivity to crystalline and amorphous phases is similar. Rietveld refinement can resolve these uncertainties. Rietveld refinement is regarded as an interesting method to accurately analyze two-dimensional scattering data. As such, Rietveld refinement includes all crystalline diffraction peaks and accurately fits the crystalline contribution.	[72,132,133]
NMR	NMR identifies small variations in the degree of magnetic field shielding for a specific atom with regard to surrounding atoms and thus provide critical information needed to elucidate the structure properties. In crystalline solids, equilibrium bond angles and distances vary due to the packing structure.	The 13 C T1 parameter in solid-state NMR, sensitive to amorphous and crystalline parts, is time-consuming for routine analysis.	[134,135]
IR	A vibration spectrum is produced from the absorption/emission of electromagnetic radiation at frequencies corresponding to the vibration of specific chemical bonds. Vibration energy states corresponding to the quantum mechanical states of electron waves for specific chemical bonds are determined by the equilibrium bond strength, geometry, and reduced mass of the atoms. In solid materials, the packing structure of molecules affects the equilibrium energy states. Structural information of crystalline structures is provided by small changes in vibration peak position/intensity.	The presence of hemicellulose, pectin, and lignin might interfere with cellulose vibration peaks, thereby leading to misinterpretation of the results.	[134]

XRD characterization of cellulose recovered from sugarcane bagasse and its conversion to nanocellulose using ball-milling-assisted-acid hydrolysis showed that high acid treatment (ball-milling for 12 h with 40% sulphuric acid) produced nanocellulose of higher crystallinity (86.1% compared with 71.1% for nanocellulose obtained by ball-milling for 12 h with 20%

sulphuric acid).[67] Comparison of the crystallinity of treated and untreated material showed that crystallinity significantly increased as a result of chemical and/or mechanical treatment (Table 9). As such, an increase in crystallinity from 60% to 69% was observed for bleached fique fiber, [68] from 62% to 81% for treated date palm sheath fiber, [69] from 55.8% to 81.2% for treated sugar palm fiber.[46] In the recovery of cellulose nanofibrils from pineapple leaf fibers, it was explicitly demonstrated that crystallinity index increased gradually after each treatment, i.e., 57%, 62%, 63%, 65%, and 77%, for raw pineapple leaf fibers, alkaline treated material, bleached material, acid hydrolyzed material, and nanocellulose obtained following ball milling for 3 h, respectively.[70] The increase in crystallinity has been linked to the elimination of amorphous hemicellulose and lignin, as well as, the rearrangement of crystalline domains in ordered structures.[71]

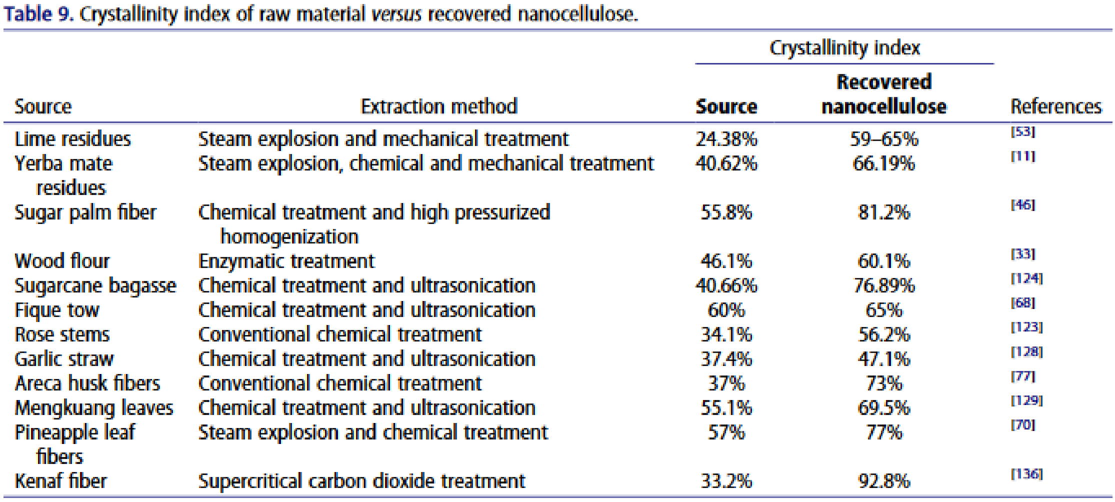


Table 9. Crystallinity index of raw material *versus* recovered nanocellulose.

Source	Extraction method	Crystallinity index: Source	Crystallinity index: Recovered nanocellulose	References
Lime residues	Steam explosion and mechanical treatment	24.38%	59–65%	[53]
Yerba mate residues	Steam explosion, chemical and mechanical treatment	40.62%	66.19%	[11]
Sugar palm fiber	Chemical treatment and high pressurized homogenization	55.8%	81.2%	[46]
Wood flour	Enzymatic treatment	46.1%	60.1%	[33]
Sugarcane bagasse	Chemical treatment and ultrasonication	40.66%	76.89%	[124]
Fique tow	Chemical treatment and ultrasonication	60%	65%	[68]
Rose stems	Conventional chemical treatment	34.1%	56.2%	[123]
Garlic straw	Chemical treatment and ultrasonication	37.4%	47.1%	[128]
Areca husk fibers	Conventional chemical treatment	37%	73%	[77]
Mengkuang leaves	Chemical treatment and ultrasonication	55.1%	69.5%	[129]
Pineapple leaf fibers	Steam explosion and chemical treatment	57%	77%	[70]
Kenaf fiber	Supercritical carbon dioxide treatment	33.2%	92.8%	[136]

The crystallinity index of Avicel, cotton linter, softwood pulp, hardwood pulp, and α-cellulose has been determined using XRD, NMR, and FT-IR.[72] For all the methods used, the same pattern was observed, i.e., crystallinity index value was highest for cotton linter and lowest for α-cellulose. However, values recorded for the different methods were different, implying that crystallinity index estimated using different methods cannot be directly compared. The authors also reported that the crystallinity index values from NMR (58, 65, 52, 45, 44% for Avicel, cotton linter, softwood pulp, hardwood pulp, and α-cellulose, respectively) were lower than the values calculated from XRD data (70, 72, 84, 81, 48% for Avicel, cotton linter, softwood pulp, hardwood pulp, and α-cellulose, respectively). This difference was related to the sensitivity of these two methods. XRD is sensitive to the crystalline domains, but less sensitive to the amorphous domains and differentiates between amorphous and crystalline regions of molecule while NMR is sensitive to both domains .[72]

Thermal stability of nanocellulose

Thermogravimetric analysis (TGA) evaluates the decomposition of material by heat which leads to the breakdown of chemical bonds .[73] Moreover, assessment of the thermal stability is crucial for further applications. TGA graphs, showing the difference in weight *versus* temperature, present weight loss around 100°C caused by the evaporation of water while cellulose pyrolysis occurs around 300°C .[74] Nanocellulose degradation occurs at higher temperature due to the formation of solid crystalline structure .[75] Incorporation of crystalline cellulose (5.5 nm, 70.25% crystallinity index) recovered from peanut oil cake significantly improved the thermal stability of pineapple/flax natural fiber composites (from 431.33-532.93°C to 478.83–634.56°C).[76] Nanocellulosic material showed degradation at higher temperature compared to the raw material (Table 10). This could be explained by the higher thermal stability of isolated nanocellulose, as compared to hemicellulose, pectin, and lignin which have lower degradation temperature and are still present in the raw material .[70] Thermal stability reflected by degradation temperature increased at the different stages of the extraction process and this could be related to the thermal stability associated to crystallinity of nanocellulose.[77]

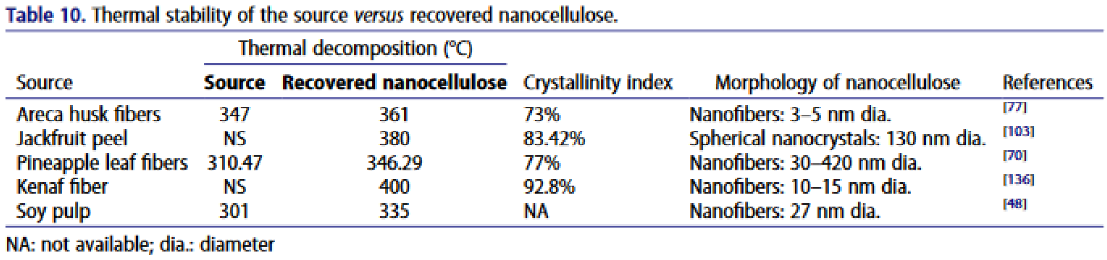


Table 10. Thermal stability of the source *versus* recovered nanocellulose.

Source	Thermal decomposition (°C) **Source**	**Recovered nanocellulose**	Crystallinity index	Morphology of nanocellulose	References
Areca husk fibers	347	361	73%	Nanofibers: 3–5 nm dia.	[77]
Jackfruit peel	NS	380	83.42%	Spherical nanocrystals: 130 nm dia.	[103]
Pineapple leaf fibers	310.47	346.29	77%	Nanofibers: 30–420 nm dia.	[70]
Kenaf fiber	NS	400	92.8%	Nanofibers: 10–15 nm dia.	[136]
Soy pulp	301	335	NA	Nanofibers: 27 nm dia.	[48]

NA: not available; dia.: diameter

Morphological characterization of cellulose

Electron microscopy is used to observe the physical characteristics (roughness, shape, and size) of cellulosic materials at nanoscale. The two generic techniques, namely, high-resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM) generate highly focused electron beams which collide with the specimen inside a vacuum chamber; SEM examines surface morphology while TEM can unravel internal structures as well.[78] TEM was used to visualize cellulose nanocrystals recovered from cellulose microfiber isolated from sunflower oil cake at different hydrolysis time, namely, 15 and 30 min. Both cellulose nanocrystals were needle-shaped but exhibited a significant difference in diameter and length, i.e., 9 nm and 354 nm for cellulose nanocrystals recovered after 15 min hydrolysis and 5 nm and 329 nm for cellulose nanocrystals recovered after 30 min hydrolysis.[79] Meng et al.[80] reported the isolation of cellulose nanofibrils and nanocrystals from liquefied banana pseudo-stem residues, explicitly showing that nanofibrils form an entangled network while nanocrystals form individual needle-like particles with less aggregation. The conversion of cellulose nanofibrils to nanocrystals arise from hydrolysis of amorphous regions, cutting long nanofibrils into shorter, needle-like nanoparticles which are the crystalline domains. Atomic force microscopy (AFM) uses a sharp tip which acts as a probe to interact with the external sample surface in order to map the physical features with nanometric precision and also quantifies the interaction among the individual structures.[81] Fig. 6 shows the SEM, TEM, and AFM of cellulose nanocrystals and cellulose nanofibrils.

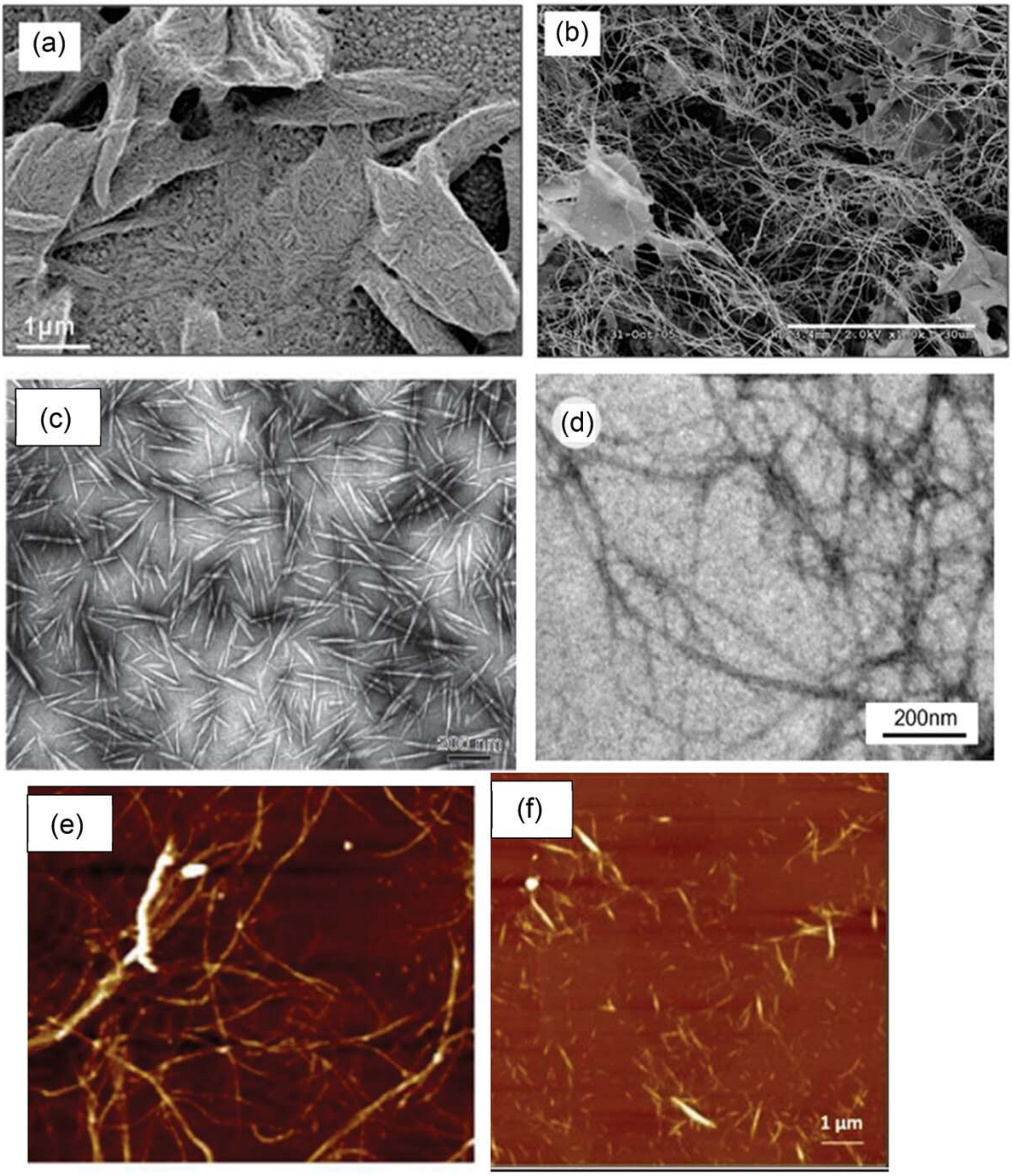


Figure 6. SEM of cellulose nanocrystals (a), cellulose nanofibrils (b)[58]; TEM of cellulose nanocrystals (c)[61] and cellulose nanofibrils (d)[57]; AFM of cellulose nanofibrils (e)[46] and cellulose nanocrystals (f)[82].

Rheological properties of nanocellulose

Nanocellulose have been reported to be excellent rheological modifiers, thereby possessing a crucial function in improving the processability of composite materials, particularly in high shear rate operations, such as, extrusion and injection molding .[83] Nanocellulose rheological characteristics depend on several factors, including, the microstructure, surface charge of particles, amorphousness, crystallinity, concentration, as well as, the pH, ionic strength, and temperature of the matrix .[84] Therefore, assessing the rheological properties of nanocellulose isolated from agro-industrial waste using different extraction methods is crucial in order to understand their behavior within the composites. A recent study carried out by Perzon ad colleagues[34] reported the rheological properties of cellulose nanofibers isolated from sugar beet waste. Different methods were used for the recovery of cellulose nanofibers, namely, chemical, enzymatic, and controlled pH enzymatic treatments. They reported that the storage modulus for cellulose nanofibers recovered by controlled pH enzymatic treatment was 2.7 times higher than cellulose nanofibers recovered by chemical treatment, supporting that cellulose nanofibers recovered by controlled pH enzymatic treatment formed a more elastic and stronger gel. Differences in the rheological properties were related to the amount of pectin remaining following enzymatic treatment as compared with the chemical treatment. Addition of cellulose nanocrystals recovered from *Miscanthus* fibers to starch-based nanocomposite film was associated to an increase in Young's modulus and tensile strength, therefore reinforcing mechanical strength.[85] Suspensions of cellulose nanofibers recovered from *Eucalyptus globulus* kraft pulp using TEMPO-oxidization were assessed at different concentrations and pH. Increasing cellulose nanofibers concentration formed stronger gels, while acidic pH enhanced aggregation caused by lower charge repulsion between nanofibers, thus increasing viscosity of suspensions .[86]

Application of nanocellulose

The abundance, non-toxic characteristics, mechanical properties, and biodegradability of nanocellulose make it an attractive material for application in various fields. To date, nanocomposite materials find application in multiple sectors, namely, the food industry, as biodegradable food packaging, texturing agent; in the medical field, as wound dressing, for controlled drug delivery, blood vessel replacements, scaffold design for bone regeneration, reinforcing agent in dental restorative material; in the cosmetic industry, as thickener, moisturizing mat, masks; in polymeric reinforcement, as a reinforcing filler in rubber; improved performance and flexural strength of cement paste; energy applications, as semitransparent electrode recyclable solar cell.[13,87–89] Table 11 summarizes the uses as well as the specificities of nanocellulose extracted from agro-industrial by-products.

The development of biodegradable food packaging stems from the urgent need to reduce pollution andconsiderable effort has been devoted in this regard. Continued effort to hone and adjust the concept of biodegradable food packaging is key to meet environmental and societal requirements. A number of criteria, such as, acidity, food media (wet, dry, fatty), should be considered while formulating biodegradable food packaging. Recently, a group of researchers reported that the reinforcement of acetylated hemicellulose films with acetylated nanocellulose, minimized the hydrophilicity and solubility in food simulants .[90] Nanocellulose confers enhanced mechanical properties to food packaging films. Incorporation of nanocellulose crystals (8%) to gelatin, chitosan, starch based nano composite films showed improved Young modulus, elongation, and tensile strength at break due to agglomeration and cellulose-cellulose physical interactions.[91] Cellulose nanocrystals (5 wt%) isolated from pea hull added to carboxymethyl cellulose film produced a reinforced film possessing enhanced tensile and water vapor barrier properties (50.8% higher and 53.4% lower, respectively, compared to pure carboxymethyl cellulose film).[92] Nanocellulose having a higher water content has been successfully used to reduce fat levels in hamburgers, cheese, sausages, and baked food, thereby advocating the use of nanocellulose as a functional ingredient to produce low calorie foods.[93] Nanocellulose can improve the quality of specific foods, such as, starch

Table 11. Application of nanocellulose recovered from agro-industrial by-products.

Application	Source	Specificity	References
Cosmetic	Nanocellulose from *Canarium ovatum* pulp	Nanocellulose suspension (absorption peaks from 250 to 300 nm) from *Canarium ovatum* pulp showed optical properties in the same range as nano-TiO_2 particles (absorption peaks from 356 to 428 nm), which are used included into concealers and sunscreens cosmetic products.	[96]
Drug delivery/medical applications	Cellulose nanofibers from medical grade cotton	A nanocellulose film coated with honey and polyvinylpyrrolidone as binder was designed. Nanocellulose film incorporated with honey significantly inhibited Gram positive and Gram negative bacteria, suggesting that the film might act as a good wound dressing.	[137]
	Cellulose nanofibrils from sugarcane bagasse	Cellulose nanofibrils-alginate grids showed lateral expansion after printing and contracted upon cross-linking of calcium ions. Release of calcium ions from the cellulose nanofibrils and cellulose nanofibrils-alginate constructs was measured in order to assess the ability of cellulose nanofibrils to act as carrier for calcium ions. With the help of 3D printing, this concept allows personalization of wound dressing, *i.e.*, tailor-made dressings which can adapt to specific shape based on wound healing treatment.	[138]
Food related/biodegradable plastic	Acetylated nanocellulose from wheat straw	Hydrophilicity and solubility of film made from acetylated nanocellulose coupled and acetylated hemicellulose coated with polycaprolactone was reduced by increasing the degree of acetylation. Film designed were least soluble in fatty food systems, suggesting possible application in non-water-based systems and dry storage.	[90]
	Nanocellulose from *Eichhornia crassipes*	Biocomposite from *Eichhornia crassipes* nanocellulose and *Pachyrhizus erosus* starch showing thermal stability and low moisture absorption, was biodegradable. Thus, suggesting possible application as environmentally friendly plastics for food packaging.	[139]
	Oxidized nanocellulose from *Phoenix dactylifera* L. sheath fibers	Chitosan bionanocomposite films containing oxidized nanocellulose from *Phoenix dactylifera* L. sheath fiber showed higher tensile strength compared to films made from Chitosan only. Chitosan/ oxidized nanocellulose bionanocomposite films possessed good moisture barrier and thermal stability properties.	[69]
	Nanofibrillated cellulose from *Arenga pinnata* fibers	Bionanocomposites prepared from *Arenga pinnata* nanofibrillated cellulose and *Arenga pinnata* starch possessed higher tensile strength and modulus values compared to *Arenga pinnata* starch only, but displayed low elongation. Good dispersion of *Arenga pinnata* nanofibrillated cellulose within the *Arenga pinnata* starch, interesting adhesion and barrier properties, advocates for the use of the bionanocomposite for short-life packaging applications.	[45]
Green tire technology/natural rubber compounding	Nanocellulose from rice husk	Composite prepared from carbon black and rice husk nanocellulose showed low rolling resistance, which is associated to reduced fuel consumption and carbon emission	[140]
	Nanocellulose from dried rubber tree leaves	The tensile strength, tensile stress, and elongation at break of rubber nanocomposites increased with addition of cellulose nanocrystals. Cellulose nanocrystals interaction within the molecular chain offer higher stiffness, thus contributing to the reinforcing effect.	[141]

foods. Addition of nanocrystalline cellulose prevents retrogradation due to the formation of hydrogen bonds between amylose starch and hydroxyl groups of nanocrystalline cellulose.[94]

The biocompatibility and non-toxicity of nanocellulose have increased its interest for medical applications. Cellulose nanofibers used for the encapsulation of drug by spray drying produced microparticles which formed a tight fiber network, thus sustaining drug release and limiting drug diffusion.[95] The use of nanocellulose in cosmetics has been proposed in order to circumvent toxicity issues related to the use of metal oxide nanoparticles.[96] In addition, it can be argued that the use of nanometric cellulose is in line with current demand for naturally derived cosmetic products. Nanocellulose have been also praised for their function as reinforcing components of composite materials. Nanocellulose enhances intra fiber and fiber-matrix interactions within the composite system, thereby increasing the strength and stiffness of the material.[32] Nanocellulose possesses large specific surface area, high aspect ratio (length by breath ratio), and exhibit better mechanical properties compared to micro cellulose.[97] The high crystallinity and hydrogen bonding ability of cellulose nanocrystals are considered to be interesting features contributing to the excellent barrier properties of nanocomposite film network consisting of cellulose nanocrystal. Besides, cellulose nanocrystals enhance the crystallinity of nanocomposites, resulting in higher tortuosity, while good dispersion improves mechanical performance.[58] Nanocellulose as a promising nanofiller improves the functional properties of composites, including, the thermal, mechanical, and barrier properties .[58] Another advantage of using nanocellulose instead of micro cellulose as filler in polymer matrix the preservation of transparency due to the homogeneous distribution and dispersion of nanocellulose within the polymer matrix.[97] Cellulose nanocrystals meet the increasing demand low-cost pickering stabilizers. The size, high aspect ratio, large elastic modulus, as well as the hydrophilic face and hydrophobic edge plane of cellulose nanocrystals contribute to the amphiphilic nature of the molecule, which are beneficial for stabilizing emulsions .[98] Cellulose nanofibrils were reported to form a network at oil/water interface, thus encapsulating oil in nanocellulose shell, preventing coalescence of oil droplets and forming stable emulsion .[99]

Concluding remarks

The groundbreaking studies on nanocellulose, the multiple advantages of the material, as well as the increased perspectives for applications, underpin the need for compiling recent scientific data regarding the potential of agro-industrial by-products as cellulose reservoirs for production of nanocellulose. Moreover, various studies reporting the recovery of cellulose from different agro-industrial wastes highlight the tremendous potential of recycling in order to mitigate issues associated to waste disposal. However, conventional cellulose extraction involves the use of toxic/hazardous chemicals, such as, sodium hydroxide, sodium chlorite, and sulphuric acid. In addition, the pre-washing, washing after alkaline, bleaching, and acid hydrolyzing treatments produce a lot of toxic effluents.

Green extraction technologies offer multiple advantages over conventional extraction methods. As such, in line with ecological and sustainable concepts, improvements in cellulose recovery using ultrasound and steam explosion can reduce the treatment time and the amount of energy required. Using mild acid for example might reduce the amount of water required to adjust the pH of the material to neutral. Deep eutectic solvents have been recommended as eco-friendly chemicals of extracting cellulose from plant material. High-pressure homogenization, ball milling, and ultrasonication are used instead of acid hydrolysis. However, high capital investment and training cost might be major limitations to implementation of these cutting-edge technologies. More studies are required to assess the effectiveness of novel techniques, such as, deep eutectic solvents, in the recovery of nanocellulose from different agro-industrial waste. Process optimization using statistical approaches, such as, response surface methodology enables the determination of optimal conditions required for effective recovery of nanocellulose from selected agro-industrial waste.

At laboratory scale level ultrasonication and high-pressure homogenization seem to produce higher yields. However, it is noteworthy highlighting that the yield also depends on the initial amount of cellulose present in the raw material. Besides, several studies did not specify the extraction yield which is key while considering large scale recovery of nanocellulose from specific agro-industrial by-products. Additionally, determining the physico-chemical characteristics, for instance, crystallinity index, purity, thermal stability, of nanocellulose is crucial to gauge the impact of the extraction process on the physico-chemical modifications of nanocellulose. Drying method was found to affect the morphological properties of nanocellulose. Spray drying has been advocated as the most suitable method to dry nanocellulose suspension in order to provide dry nanocellulose required for material application as well as to reduce bulk associated to transportation of aqueous nanocellulose suspension while supercritical drying and freeze drying of nanocellulose produced highly networked structures.[100]

Although, significant progress has been made regarding cellulose extraction and nanocellulose isolation from agro-industrial by-products, more work needs to be done to improve the concept. Bacteria cellulose might be advocated to be an interesting alternative since it involved a bottom up approach and requires less energy and chemicals. The successful implementation of nanocellulose production using green technologies at industrial scale requires decades of intensive research.

Acknowledgments

The authors acknowledge Carnegie Corporation of New York, Future Africa and the Early Career Research Leader Fellowship Program, the DST/NRF Centre of Excellence in Food Security, European Union's Horizon 2020 research and innovation programme (grant agreement number 862170).

Funding

This work was supported by the Carnegie Corporation of New York [G 17-55192]; DSI-NRF Centre of Excellence in Food Security [91490]; EU horizon 2020 research and innovation programme grant No. 862170.

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