

“CELLULOSE NANOCRYSTALS IN FOOD INDUSTRY”

Soumya Hiregoudar

Ph.D. Food Science and Nutrition, University of Agricultural Sciences, GKVK, Bengaluru

Email: soumyashiregoudar@gmail.com

Phone number: 8073562812

Abstract

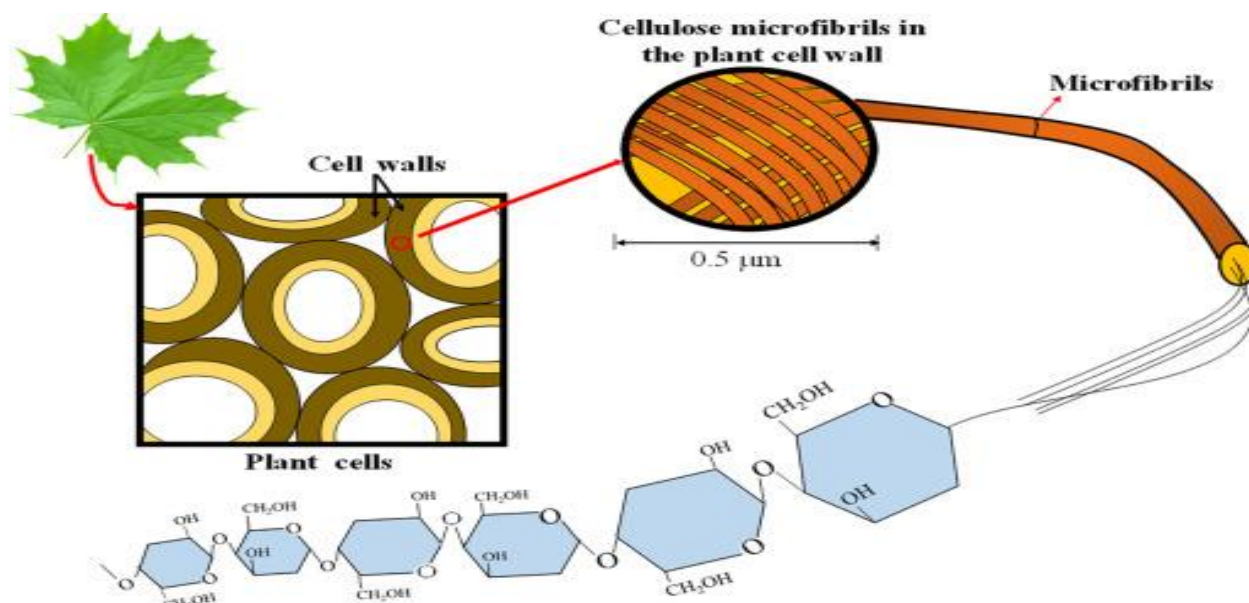
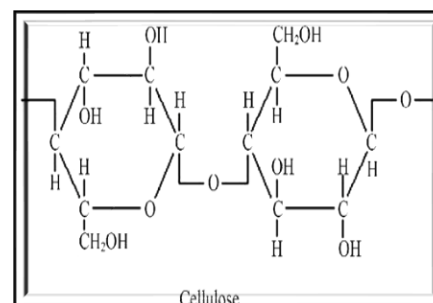
Cellulose, a macromolecule polysaccharide is most **broadly dispensed** in plants, fungi, **micro organism** and marine animals. Nanocellulose is a **time period relating to nano-dependent** cellulose. This **can be both** cellulose nanofibers (CNF), cellulose nanocrystals (CNC) or bacterial nanocellulose (BNC). CNC, a **period of one hundred nm**, **consists** of nanocelluloses with alternating crystalline **domain names** with rod like structures, **received with the aid of using distinctive** isolation **strategies** like acid, alkali and enzymatic hydrolysis. The cellulose nanocrystals have **incredible bodily** and chemical **houses** and are **taken into consideration** as novel **meals element** and biodegradable packaging **substances** in **meals** industry, used as a thickeners, flavor carriers, suspension stabilizers in a **extensive type of meals merchandise** and in **utility** of **transport** system. Based on its small size, **huge floor** area and **excessive** crystallinity, cellulose nanocrystals **famous incredible** mechanical **houses**, **excessive** thermal stability, **energetic** chemical **response houses**, and the rheological **houses**.

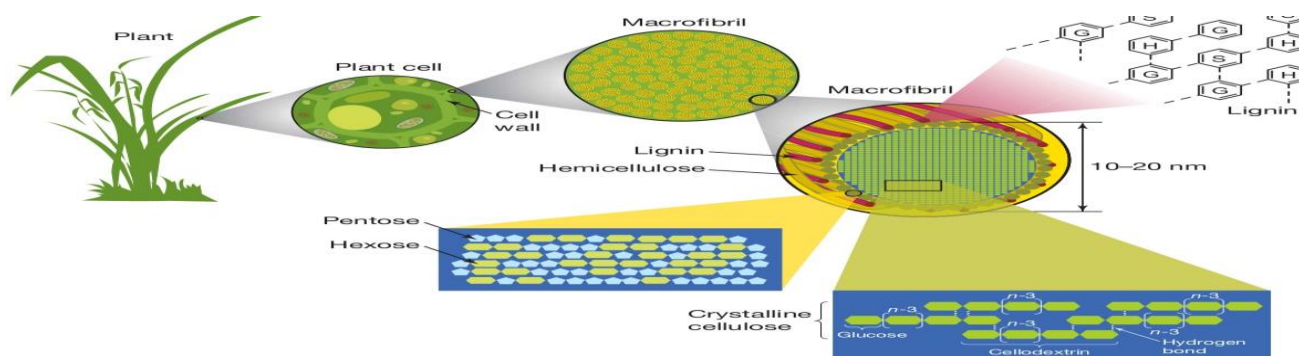
Key words : Cellulose, Nanocrystals, Food industry

Introduction

Cellulose

- Cellulose was first discovered by Payen.
- Present in plant cell wall at around 30 -50%.
- Two forms of cellulose(crystalline and amorphous).
- It is composed of β 1,4 – linked glucopyranose units.





Cellulose present in the cell wall of plants in the form of cellulose microfibrils. Figure 1 shows the chemical structure of cellulose.

Plant **mobileular partitions** are **complicated systems made out of various** configurations of interlocking polysaccharides. Fig 2. **indicates** the simplified **shape** of the **mobileular wall** and the cellulose **association within side the plant mobileular**. Based on its **shape** and composition, the **mobileular wall is split into 3 special layers**: the **center lamella (ML)**, the **number one wall (P)**, and secondary wall. The ML **carries a excessive quantity** of lignin and is **on the whole chargeable** for binding the neighbouring cells. The **number one wall is about 30-one thousand nm** thick and **carries 3 fundamental** components-cellulose, hemicellulose, and pectin-**in which** cellulose microfibrils (MFs) are **organized** crosswise. The secondary **mobileular wall** is further divided into **3 layers**, the outer (S1), **center (S2)**, and inner (S3) layers, which **range of their microfibrils' attitude** with **admire** to the fibre axis [21]. Among all, the S2 layer is the **maximum precious** and **carries the best quantity** of cellulose.

Types of cellulose

There are **4 one-of-a-kind** polymorphs of cellulose: cellulose I, II, III, and IV. Cellulose I is **local** cellulose, i.e., **determined** in nature, and it **takes place** in allomorphs, $I\alpha$ and $I\beta$. Cellulose II is **additionally known** as regenerated cellulose; **it's far** the **maximum solid shape** of crystal, and emerges from aqueous sodium hydroxide **remedy** of cellulose I. The **feature difference among those kinds** of cellulose lies in the **format in their** atoms: the chain in cellulose I is in parallel direction, **while it's far determined** to be antiparallel in cellulose II. Cellulose III and IIII **may be received through** ammonia **remedy** of cellulose I and II, respectively, **while**, cellulose IV is derived from the **change** of cellulose III.

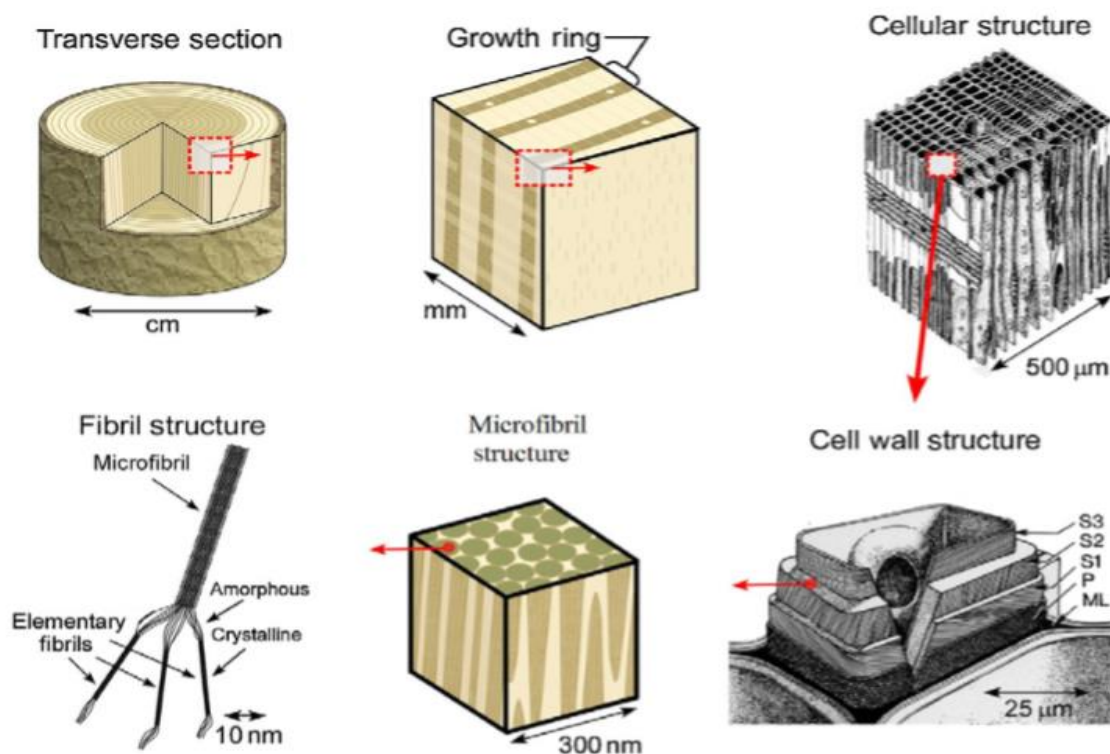
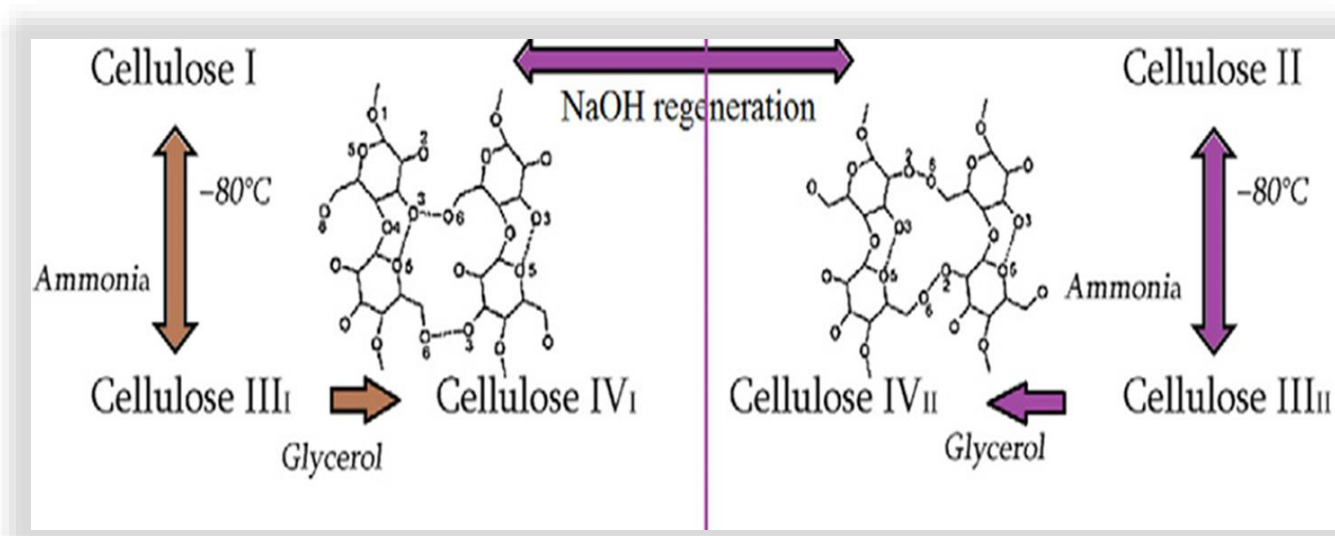


Figure 2: Transection view of cell wall

Nanocellulose



Why nano?

The size reduction enables new opportunities for the development of innovative nano systems and nanostructured materials.

Particle of any shape with dimensions < than 100 nm

Properties of nano particles

Very powerful; wide area; and very reacting, Less Defect, Thermal steadiness, Distinctive optical, electrical, and magnetic characteristics

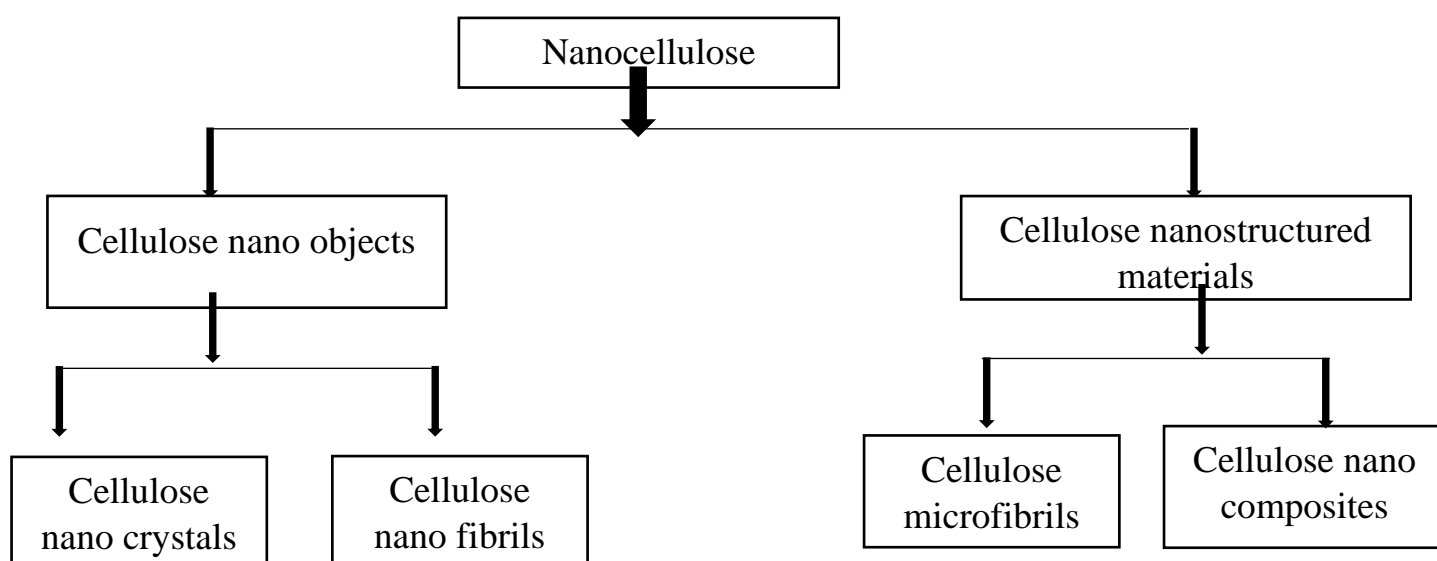
Why cellulose?

A sustainable material: high availability, natural & renewable, economic, non-toxic, biocompatibility and biodegradability

Properties of nano particles

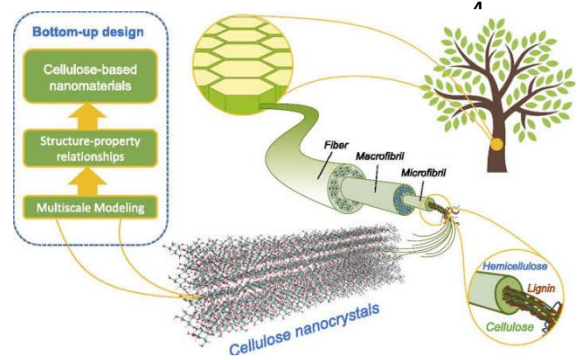
High strength and modulus, flexibility, and light weight, Charged with electricity, Reactive to chemicals, Dimensional steadiness, Water assimilation, Barrier characteristics, Low aspect ratio, Transparency and opacity

Classification of nanocellulose



Cellulose nanocrystals

- Cellulose nanocrystals are nanoscale celluloses extracted from **herbal** Nanofibers.
- Organized **shape** of strongly ordered crystalline particles.
- Rod like crystalline particles.
- Crystalline index above 75%.
- Rectangular in **pass** section.
- These are **fashioned with the aid of using the usage of distinct** isolation methods (acid hydrolysis, mechanical method)



Sources of cellulose nanocrystals

Animal excrement and plants

Industrial wastes like fruit and vegetable peels include 10–30% cellulose, as do agricultural and industrial wastes like rice husks and oat husks, which contain 30–60% cellulose on average. Regarding the extraction of polysaccharide and NC, a variety of plant materials are being researched, including wood, rice husk, sisal, hemp, flax, kenaf, and coconut husk.



Bacteria

There is only cellulose in bacteria. Compared to plant nanocellulose, it has a great capacity to retain water. Because it lacks lignin and hemicellulose, the extraction process is easier than with plant nanocellulose.

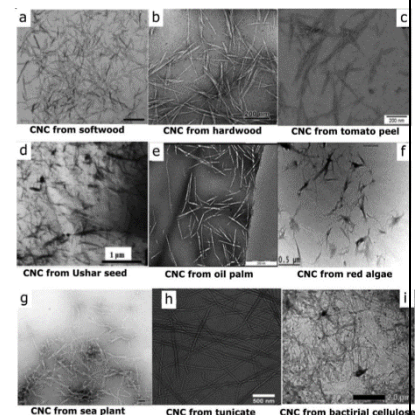
Bacterial cellulose (BC) is a byproduct of some bacteria's basic metabolic operations. *Gluconacetobacter xylinus* is the most frequently seen species of BC-producing bacteria.

Algae :

Among red, green, yellow algae, red algae has more content of cellulose.

Tunicates:

Tunicates are marine invertebrate animals. Tunicate cellulose **consists of just about natural** cellulose of C1 β allomorph **kind** with **excessive** crystallinity.



Hierarchical arrangement of cellulose nanocrystals

Cellulose undergo spinning in hierarchical arrangement in which cellulose present in the form of fibers. Through some of isolation process it convert into cellulose microfibrils and again through acid hydrolysis it converts into cellulose nanocrystals.

Bottom up design

Understanding of cellulose nanomaterials through multiscale modelling with the guidance of bottom up design to know the structure property relationships of cellulose based nanocrystals.

Properties of cellulose nanocrystal

- High strength and modulus
- High surface area and aspect ratios, High thermal stability, Strong water binding ability, Possibilities for modifying chemicals, Ecological disposal or recycling at the end of life, Ecologically sound natural materials

Methods of isolation of cellulose nanocrystals

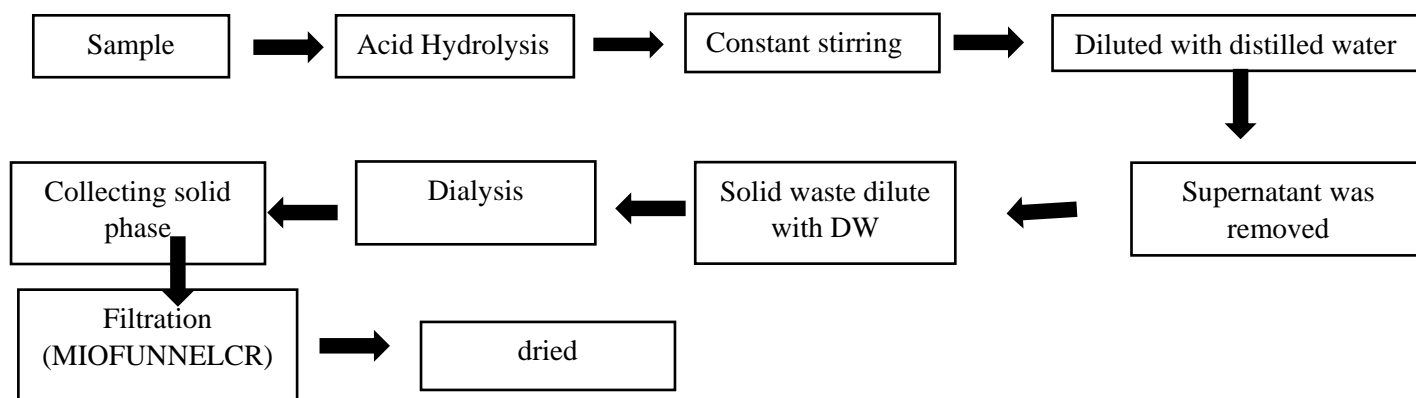
Pre-treatment methods: Enzymatic hydrolysis, Alkali method, Ionic method

Chemical hydrolysis: H₂SO₄ hydrolysis, HCL hydrolysis

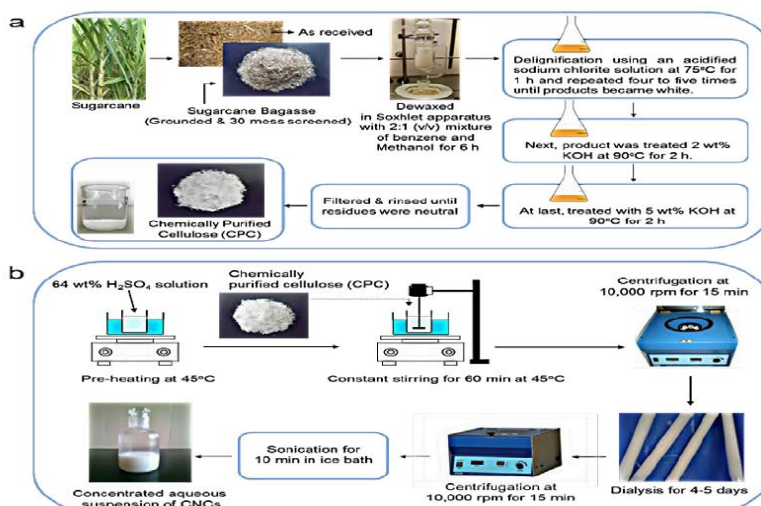
Mechanical method: High pressure, Grinding, Cryocrushing, Ball milling

1. Acid hydrolysis:

To **launch** CNCs, acid hydrolysis of purified cellulosic **fabric** is **carried out** using **robust** mineral acids **below managed** temperature, time, agitation, and acid/cellulose ratio conditions. Different mineral acids **may be** used for this purpose, **along with** sulfuric, hydrochloric, phosphoric, maleic, hydrobromic, nitric and formic acids. Sulphuric acid is the **maximum notably** used acid for CNC preparation. During hydrolysis, disordered amorphous **domain names** and **nearby** interfibrillar contacts of cellulose are preferentially hydrolysed, **while** stable crystallites **continue to be** intact and **may be removed** as rod-like nano crystalline particles. The CNC dispersion in a **robust** acid is diluted with water and washed using successive centrifugations. Neutralization or dialysis with distilled water is performed to **cast off loose** acid from the dispersion. Additional steps **along with** filtration, centrifugation or ultra-centrifugation, **in addition to** mechanical or ultrasound disintegration.



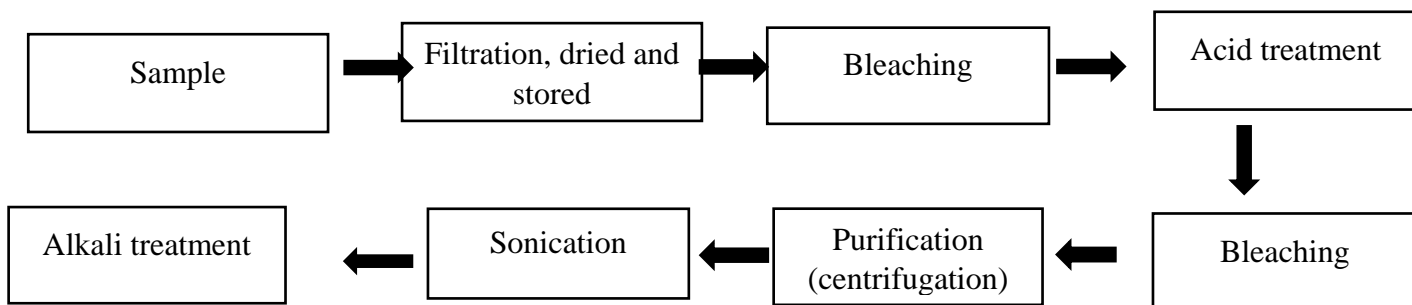
Example :



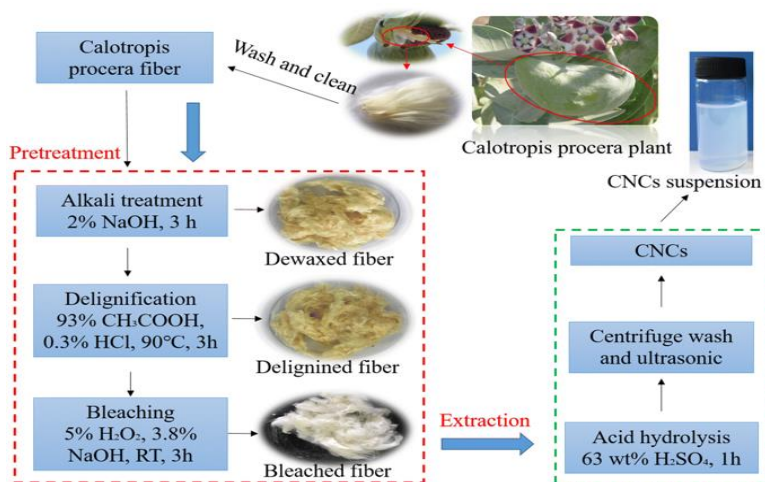
2. Acid alkali pre-treatment

This pre-treatment **consists of 3** steps

- (i)soaking of plant fibers in 12–17. **five** wt% sodium hydroxide for 2h, **so one can growth** the fiber **floor location** and to make the fibers **extra at risk of** hydrolysis
- (ii)Treatment of the fibers with 1M HA at 60–80°C **so one can** hydrolyse the hemicelluloses
- (iii)Treating the fibers with 2 wt% NaOH **answer** for 2h at 60–80°C to disrupt the lignin structure. After such pre-treatment, the cellulose **content material** increases from 43% to 84%.



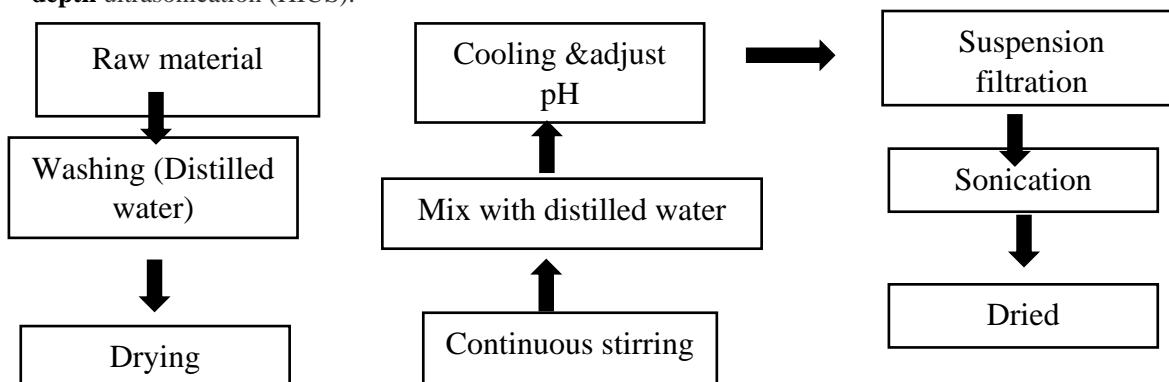
Example:

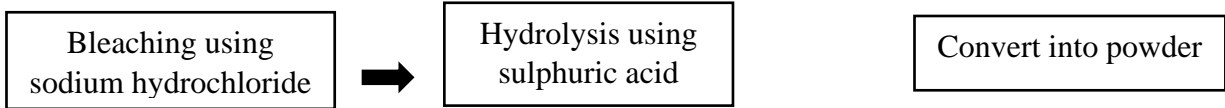


3. Mechanical treatment

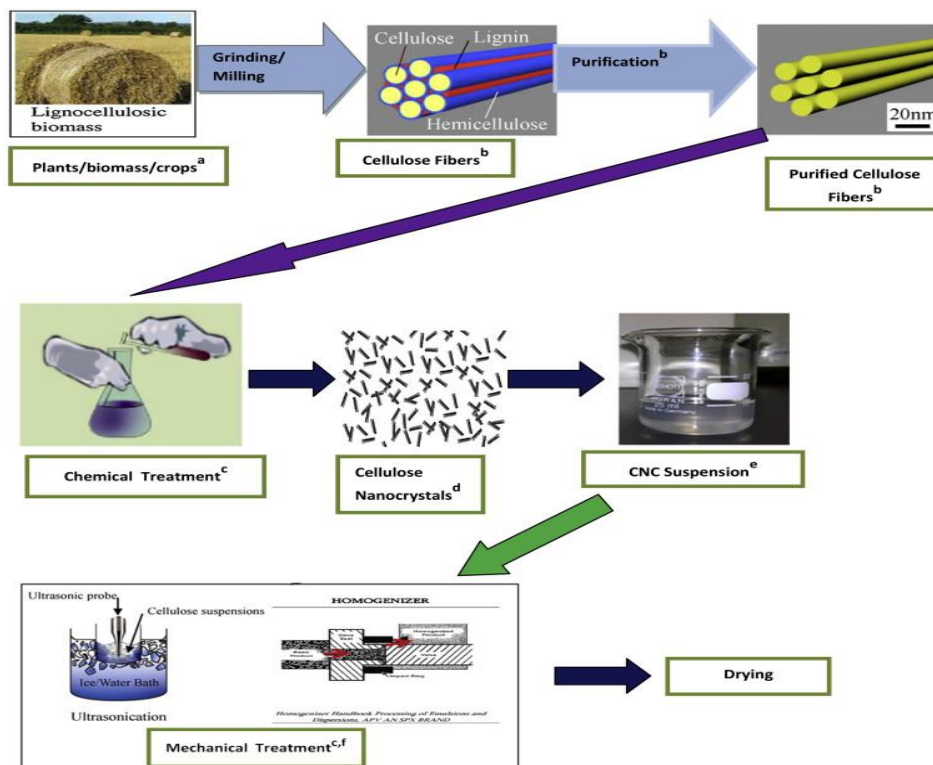
Cellulosic **substances** are required to **undergo** mechanical **remedy** for defibrillation. Pre-remedy processing, **both via way of means of chemical compounds** or enzymes, is **finished earlier than** mechanical **traumatic inflammation** to ease the process.

Chemical **remedies assist in** widening the **distance among** hydroxyl groups, **growing the internal floor, changing** crystallinity, and breaking cellulose hydrogen bonds, **as a result improving floor areas**, which **allows improve** the reactivity of the fibres. There are many mechanical **strategies** for converting cellulosic fiber to nanocellulose, **inclusive of** homogenizing, micro-fluidization, grinding, crycrushing, and high-**depth** ultrasonication (HIUS).





Example :

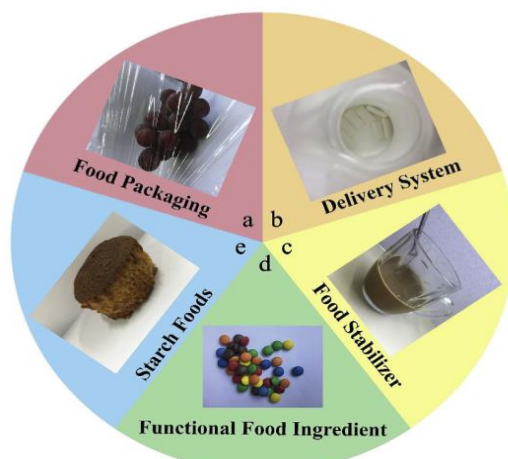


Size of cellulose nanocrystals

Source	Preparation method	Length(nm)	Width(nm)	Aspect ratio(L/D)
Wood	H ₂ SO ₄ hydrolysis	100-300	3-5	20-100
Cotton	HCL hydrolysis	100-150	5-10	10-30
Ramie	H ₂ SO ₄ hydrolysis	70-200	5-15	12
Sisal	H ₂ SO ₄ hydrolysis	100-300	3-5	60
Tunicates	H ₂ SO ₄ hydrolysis	>1000	10-20	100
Bacteria	H ₂ SO ₄ hydrolysis	100-1000	10-50	2-100

The dimensions of cellulose nanocrystals depending on the source and method of preparation

Applications of cellulose nanocrystals



Some derivatives of CNC

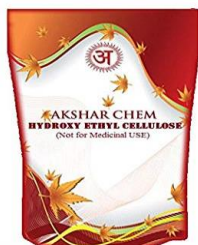
Cellulose nanocrystals - ~12% aqueous slurry



Cellulose nanocrystals - ~98% spray dried

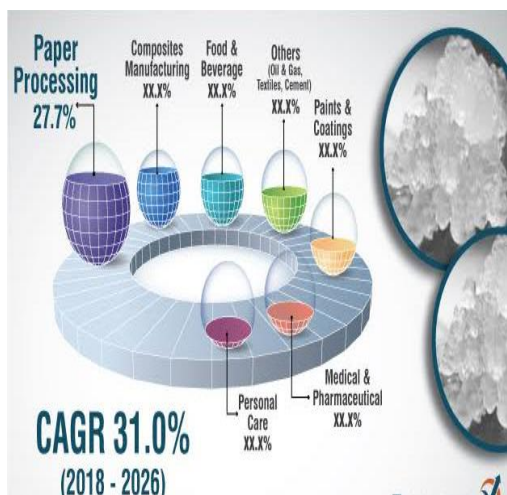


Cellulose nanocrystals - ~98% freeze dried

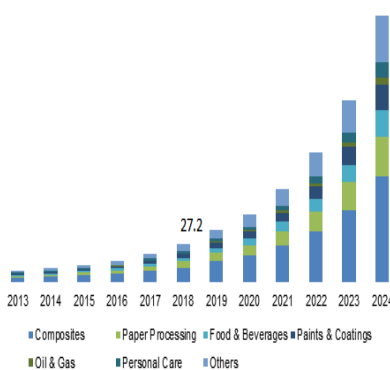


Global Nanocrystalline Cellulose Market Share (%)

By End User (2018)



Compound annual growth rate was expected at 31% at the end of 2026.



Companies that manufactures CNC

- American Process Inc.
- Blue Goose
- Hokuetsu
- NCCTM
- Plantrose
- Tech Futures
- University of Maine
- US Forest Service

Review of Literature

Trilokesh and Uppuluri. (2019) conducted a **observe** on isolation and characterization of cellulose nanocrystals from jackfruit peel. Cellulose nanocrystals (CNCs) **had been effectively remoted** from the jackfruit peel **the usage of** sodium chlorite **remedy accompanied via way of means of** sulphuric acid hydrolysis. The **general** produced cellulose **turned into** 20.08 % w/w (dry weight). The **remoted CNC had been characterised** for its morphology, functional, crystal and thermal **residences via way of means of** SEM, FTIR, NMR, HPLC and TGA. Results revealed, the presence of α -cellulose **and shortage** of other biomass fractions like hemicellulose and lignin with **excessive** crystallinity of 83.42%. Hence the **remoted** cellulose and CNCs from jackfruit peel waste **may be hired** for potential applications **withinside the discipline** of food, paper, paints, optics, pharmaceuticals, **surroundings** remediation, composite synthesis.

Extraction and characterizations of cellulose nanocrystals from pineapple peel **turned into** evaluated **via way of means of** **Madureira et al. (2018)**. Pineapple residues **had been** purified to **cast off** pigments, waxes, hemicellulose and lignin **via way of means of** bleaching for **four hr (TPP4) and six hr (TPP6)**. The **dealt with** pineapple peel (TPP4 and TPP6) **turned into** taken for extraction of cellulose nanocrystals **via way of means of** acid hydrolysis for 30 and 60 min. These cellulose nanocrystals had small sizes (< 100>)

Extraction of cellulose nanocrystals (CNC) from rice, oat husk and eucalyptus for the **manufacturing** of aerogels for **meals** packaging **utility became** investigated **with the aid of using** **oliveira et al. (2018)**. Commercial cellulose **became** used as a **manage** sample. CNC **have been acquired** from enzymatic hydrolysis and mechanical treatment. The **common** diameter of the nanocrystals **numerous** from 16.**zero** to 28.**eight** nm. The aerogels **organized** with cellulose nanocrystals **confirmed** a porous and uniform **shape** with a water absorption **potential among** 264.2% and 402.**eight**% at 25°C. The aerogel of oat cellulose nanocrystals **confirmed a bigger** pore **length and large** water absorption **potential** of the aerogels than **different** cellulose nanocrystals. These **effects confirmed** that agro-**commercial** residues have promising **packages** in **diverse commercial** fields and **may be** used as aerogel absorbers of water in **meals** packaging.

Varanasi et al. (2018) conducted a **have a look at** on the **position** of electrostatic forces **withinside the CNC capacity** to stabilize oil/water emulsions is explored **the use of** canola oil/water and hexadecane/water as **version structures**. Canola oil/water and Hexadecane/water (20/80, v/v) emulsions **have been** stabilized with the addition of CNCs **the use of** ultrasonication. Emulsion droplet **length is two** μm as measured **with the aid of using** optical microscopy. It **became discovered** that CNC can stabilize oil/water emulsions **no matter** their **rate** density. The **discount** of pH **under 2 results** in the aggregation of CNC to **shape** stable emulsion, **shape** a gel-like behaviour. The **effects indicates** that the **structures** are **absolutely** biodegradable and biocompatible **and may shape** gels, **starting** new innovation avenues in **meals** and biomedical **packages**.

Production of biodegradable starch nanocomposites **the use of** cellulose nanocrystals extracted from coconut fibre **became** studied **with the aid of using** **Cerqueira et al. (2017)**. Cellulose nanocrystals **have been** extracted from coconut fibres and **included** in manioc (cassava) and potato starch **movies** at **exclusive** concentrations. The nanobiocomposite biodegradable **movies evolved** with addition of cellulose nanocrystals exhibited **appropriate** barrier and mechanical **houses consisting of accurate** transparency, manageability, homogeneity, **good enough** solubility, and **excessive** strength. The potato starch **movie** with the **bottom** nanocrystal **attention became discovered** to **showcase** the **first-rate** mechanical **houses**.

GLOSSARY

CNC: Cellulose Nano Crystals
 PP : Pineapple Peel
 TPP: Treated Pineapple peel
 DLS: Dynamic light scattering
 SEM: Scanning Electron Emission
 NMR: Nuclear Magnetic Resonance
 ZP: Zeta Potential
 TGA: Thermogravimetric analysis
 DSC: Differential scanning calorimetry

CONCLUSION

CNC (Cellulose nanocrystal) is **specific amongst a selection of different nanostructure substances because** of its renewable, sustainable, nontoxic, and biocompatible nanomaterials in nature and having **greater packages in meals industry**. CNC **may be** used as additives, thickeners, flavor carriers, suspension stabilizers, **shipping** system, packaging system. Even **alleviated** though it is having **diverse extraordinary residences** and **excessive** availability in nature, the extraction of cellulosic **cloth** is **huge** challenge. There are **nevertheless** no common **policies** for CNC in worldwide, and **unique** human and the environmental **dangers** of CNC is **want** to be **similarly** explored. Further **studies want** to be **targeted** on their technological and **dietary residences, protection checks** and **law** for **meals** application.

References

- CERQUEIRA, J. C., PENHA, J. D. S., OLIVEIRA, R. S., GUARIEIRO, L. L. N., MELO, P. D. S., VIANA, J. D., AND MACHADO, B. A. S., 2017, Production of biodegradable starch nanocomposites using cellulose nanocrystals extracted from coconut fibers. *Polímeros*, **27**(4): 320-329.
- OLIVEIRA, J. P., BRUNI, G. P., EL HALAL, S. L. M., BERTOLDI, F. C., DIAS, A. R. G., AND DA ROSA ZAVAREZE, E., 2019, Cellulose nanocrystals from rice and oat husks and their application in aerogels for food packaging. *Int. J. of Bio. Macromolecules*, **124**: 175-184.
- GEORGE, J., AND SABAPATHI, S. N., 2015, Cellulose nanocrystals: synthesis, functional properties, and applications. *Nanotechnology, science and applications*, **8**: 45.
- MADUREIRA, A. R., ATATOPRAK, T., ÇABUK, D., SOUSA, F., PULLAR, R. C., AND PINTADO, M. E., 2018, Extraction and characterisation of cellulose nanocrystals from pineapple peel. *Int. J. of Food Studies*, **7**: 24-33.
- MARTIN-MARTINEZ, F. J., 2018., Designing nanocellulose materials from the molecular scale. *Proceedings of the National Academy of Sciences*, **115**(28): 7174-7175.
- MU, R., HONG, X., NI, Y., LI, Y., PANG, J., WANG, Q., AND ZHENG, Y., 2019, Recent trends and applications of cellulose nanocrystals in food industry. *Trends in Food Science & Technology*.
- NASIR, M., HASHIM, R., SULAIMAN, O., AND ASIM, M., 2017, Nanocellulose: Preparation methods and applications. In *Cellulose-Reinforced Nanofibre Composites*. Woodhead Publishing, 261-276.
- PHANTHONG, P., REUBROYCHAROEN, P., HAO, X., XU, G., ABUDULA, A., AND GUAN, G., 2018, Nanocellulose: Extraction and application. *Carbon Resources Conversion*, **1**(1): 32-43.
- TRACHE, D., HUSSIN, M. H., HAAFIZ, M. M., AND THAKUR, V. K., 2017. Recent progress in cellulose nanocrystals: sources and production. *Nanoscale*, **9**(5): 1763-1786.
- TRILOKESH, C., AND UPPULURI, K. B., 2019, Isolation and characterization of cellulose nanocrystals from jackfruit peel. *Scientific Reports*, **9**(1): 1-8.
- VARANASI, S., HENZEL, L., MENDOZA, L., PRATHAPAN, R., BATCHELOR, W., TABOR, R., AND GARNIER, G., 2018, Pickering emulsions electrostatically stabilized by cellulose nanocrystals. *Frontiers in Chemistry*, **6**: 409.
- The Global Market for Cellulose Nanocrystals (CNC)
[https://www.researchandmarkets.com/reports/4856575/the-global-market-for-cellulose-nanocrystals-cnc?utm_source=dynamic&utm_medium=BW&utm_code=t9h28n&utm_campaign=1322608+-+The+Global+Market+for+Cellulose+Nanocrystals+\(CNC\)+2018-2030+with+Profiles+on+11+Producers+and+3+Other+Companies&utm_exec=joca220bwd](https://www.researchandmarkets.com/reports/4856575/the-global-market-for-cellulose-nanocrystals-cnc?utm_source=dynamic&utm_medium=BW&utm_code=t9h28n&utm_campaign=1322608+-+The+Global+Market+for+Cellulose+Nanocrystals+(CNC)+2018-2030+with+Profiles+on+11+Producers+and+3+Other+Companies&utm_exec=joca220bwd)
 Transparency Market Research Analysis, 2018
<https://www.gminsights.com/pressrelease/nanocellulose-market>