

A Review on Chemical Extraction of Nanocellulose from Lignocellulosic Materials

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Abstract— Cellulose is a naturally abundant polymer extracted largely from lignocellulosic materials with several promising properties that make them an alternative to conventional polymers. Isolation of cellulose from plant cell walls and conversion of this isolated cellulose fibrils to nanocellulose is a fairly easy process and the review summarizes basic chemical treatment required for processing and functionalization of nanocellulose. The tunable surface properties, low density and nano size of cellulose make them a superior option for advanced applications.

Keywords: Cellulose, CNF, Nanocellulose, CNC

I. INTRODUCTION

Cellulose is widely found in nature as chemical aggregates of individual cellulose fibers composed of numerous homopolysaccharide chains. The building blocks of these chains are β -1,4-anhydro-D-glucopyranose monomers packed in fibrillar and semi crystalline pattern. The chains are directionally asymmetric with respect to the end groups of the monomer, and thus if one end of the chain possesses the reducing end with the hemiacetal group, the opposite end will possess the non-reducing part with the hydroxyl group. The monomers still have three free hydroxyl groups, which not only play a detrimental role in hydrogen bonding, but also provides a platform for surface modification [1].

Cellulose is a renewable, biocompatible, biodegradable and non toxic polymer largely derived from plant sources. Intramolecular hydrogen bonding of cellulose restrains its solubility in water and most of the organic solvents. However, cellulose exhibits poor thermal stability, hygroscopic characteristics, no melting and incompatibility to blend with most of the hygroscopic polymers. To overcome these limitations conversion of cellulose into nanocellulosic forms is advantageous which provides high aspect ratio, high strength and excellent stiffness [2,3].

Lignocellulosic materials are primarily composed of cellulose, hemicelluloses (a group of complex carbohydrates) and lignin (an aromatic material) and they are considered to be the main source of cellulose. Apart from that some amount of pectin, wax and impurities are also found in lignocellulosic materials. Lignin acts as a binder that holds cellulose and hemicellulose together. Lignin provides the desired strength and stiffness to the plant cell wall. Lignin is a cross-linked amorphous copolymer synthesized from three different phenylpropane monomers, i.e., p-coumaryl, coniferyl, and sinapyl alcohols. Hemicellulose is a heteropolymer of short, linear and branched chains of xylans and glucomannans. Hemicellulose forms hydrogen bonds and Van der Waal's interactions with cellulose fibrils and also cross links with lignin through ester and ether linkages.

Prior to getting accessibility to cellulose fibrils, chemical pretreatments are required as plant cell wall possesses a defensive inner structure to protect itself from microbial attack. Further, this structure contributes to hydrolytic stability and structural sturdiness of lignocellulosic materials. A chemical pretreatment facilitates the process of hydrolysis on the isolated cellulose fibrils to form the nanostructures [4].

This review mainly focuses on synthesis (through chemical route only) of two types of nanocelluloses viz. cellulose nanocrystals (CNC) and cellulose nanofibers (CNF).

II. NANOCELLULOSE

The common convention to apply the term nano based on size is also applicable to cellulose where a cellulose particle having at least one dimension in the range of 1-100 nm is termed as nanocellulose. Structure of cellulose is packed with segmental highly crystalline structures and disordered amorphous structure. In the crystalline region, the ordered and packed cellulose nanofibrils contributes in strength and stiffness while the disordered amorphous region provides flexibility in the bulk material.

A. Cellulose nanocrystals (CNCs)

CNCs are generally produced by acid hydrolysis of cellulose fibers dispersed in the water. Concentrated sulfuric acid is used for hydrolysis which cleaves the glycosidic linkages of cellulose and degrades the amorphous region leaving behind the crystalline structure. The acid hydrolyzed CNCs have rod like morphology with a diameter in the range of 3-35 nm and length between 200-500 nm. In this method, the produced CNCs have negatively charged sulfate groups at the surface.

B. Cellulose nanofibers (CNFs)

The production of CNF can be achieved through chemical methods, mechanical methods and enzymatic methods (Fig. 1). However, each method has their own limitations and combinations of these methods are considered to be suitable for production of CNFs in terms of cost and environment friendliness. In CNFs only diameter of the fiber is confined to the nanometric range of 5-50 nm while the length of nanofiber is extended up to several micrometers. This provides CNFs to have a high aspect ratio (length/diameter) which is beneficial for fabrication of composites having high end properties. Further, CNFs consist of both amorphous and crystalline regions which provide the additional flexibility [5].

Apart from nanocrystals and nanofibers bacterial cellulose, electrospun cellulose, hairy cellulose nanocrystalloid are also considered to be different forms of nanocellulose. However, the detailed discussion and

synthesis route of these variants are beyond the purview of this present review.

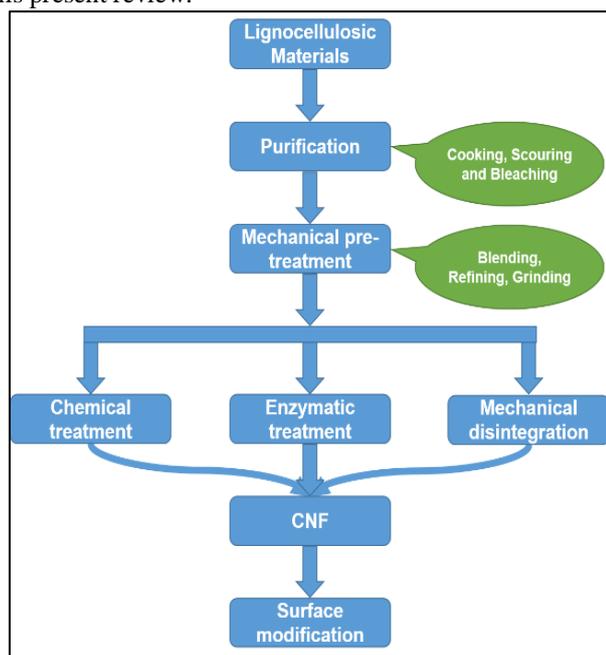


Fig. 1: Flow chart of CNF preparation route

III. EXTRACTION OF NANOCELLULOSE IN CHEMICAL ROUTE

Extraction of nanocellulose from lignocellulosic material is a two stage process. At first, non-cellulosic components such as lignin, hemicellulose and other components need to be separated by the pretreatment process. Further, cellulose fibrils are processed in several extraction methods to generate nanocellulose.

A. Pretreatment

Conventional pretreatment of lignocellulosics involves acid-chlorite treatment and alkaline treatment intending to remove non cellulosic components. Acid-chlorite treatment also known as bleaching is used for removal of lignin and other components. The reaction is carried out between 70-80° C for a varying period of time 2-12 hours depending upon the chemical composition of source material. A bright white colour is indicative of successful removal of lignin.

Alkaline treatment is carried out for removal of amorphous hemicellulose and remaining part of lignin. Different concentration of sodium hydroxide for varying time period with optional use of temperature is used for alkaline pretreatment process. The two pretreatments viz. bleaching and alkali treatment can also be coupled in a single stage for reduction in processing time and processing cost. In alkaline pretreatment process saponification of intermolecular hydrogen bonds occurs which crosslinks hemicellulose and lignin. Alkaline salt helps in substitution of ester linkages to nucleophilic acyl and forms carboxylic salt and alcohol. Apart from sodium hydroxide, potassium hydroxide, calcium hydroxide, hydrazine and ammonium hydroxides are also used for alkaline hydrolysis. However, over exposure and high concentration of alkali can degrade cellulose structure to form simple sugars.

While concentrated acid solution (~40 wt.%) is used for conversion of cellulose to nanocellulose, a dilute

acid solution (below 4 wt. %) is also a promising candidate to isolate cellulose from lignin, hemicellulose and other substances.

Delignification can also be achieved by the usage of oxidizing agents namely organic peroxidase, ozone and oxygen which cleave the ring structure under alkaline pH conditions. Oxidizing agents also enhances the efficacy of alkaline pretreatment process.

OH⁻ ions from low boiling point based organic solvents can easily be used to attack the acid ester bonds of hemicellulose and lignin. Recently, ionic liquids have been utilized for research purposes in pretreatment stages of cellulosic materials. Ionic liquids are recoverable and mild concentration of ionic liquids can easily dissolve cellulose, hemicellulose and lignin [6-8].

Some other pretreatment procedures which are followed by a mechanical disintegration process to generate CNF involves Carboxylation through 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) oxidation, Carboxylation via periodate-chlorite oxidation, Sulfonation, Carboxymethylation, and Quaternization,

In TEMPO mediated oxidation the disintegration process of cellulose nanofibril is achieved through inter molecular repulsive forces as TEMPO mediated oxidation causes carboxylation of primary hydroxyl groups which later becomes negatively charged. This results in repulsion of the nanofibers and process of disintegration get accelerated. Along with TEMPO the process requires NaBr and NaClO to achieve the oxidation process. The reaction of TEMPO with oxidants generates nitrosonium ion (⁺N=O) which converts primary alcohol to aldehyde first and finally to carboxylic groups. During drying of final product, presence of some unconverted aldehyde causes yellowing of CNFs.

Similarly, carboxylation of cellulose is carried out in combination with periodate and chlorite ions. In this method, secondary alcohol groups are converted to carboxylic groups. At first sodium or potassium periodate cleaves the cellulose structure by opening of glucopyranose ring and secondary alcohol of cellulose gets converted to aldehyde which further reacts with sodium chlorite to ensure carboxylation of cellulose surface.

Another way to introduce negative charge on cellulose surface to promote fibrillation is sulfonation in conjunction with bisulfite and periodate. The above mentioned carboxylation processes need an additional mechanical homogenizing step to obtain CNFs. Similarly, ultra-sonication, centrifugation or homogenization can also be used to carboxymethyl cellulose to ease the nanocellulose extraction process.

Grafting of positive charges on cellulose fibrils also exhibits electrostatic repulsive forces between the fibrils as with the case of grafting negative charges on cellulose surface. One of the recent approaches to cationize cellulose is grafting of quaternary ammonium groups on cellulose surface. The quaternization process is generally carried on bleached samples. Microemulsions, new solvent assisted systems are some of the recent advancements in pretreatment of cellulosic materials [4,5].

B. Conversion of cellulose to nanocellulose

With an objective to achieve high yield of nanocellulose extraction cellulosic materials are subjected to various chemical treatment methods mainly acid hydrolysis.

Utilization of concentrated mineral acids (mainly H_2SO_4 , HCl) is the oldest technique to extract nanocellulose from cellulose nanofibrils. Sulfuric acid breaks β -1,4 glycosidic linkages of cellulose and breaks the chain in narrower lengths. Further esterification of hydroxyl groups by sulfate ions facilitate in formation of a stable dispersed colloid. However, mineral acids are toxic, hazardous and corrosive. Hence, utmost care is needed during processing of nanocellulose. The process also requires extensive usage of water during neutralization of the final product.

An environmentally benign approach of hydrolysis is utilization of cellulose digesting enzymes such as cellulase which is a combination of different classes of enzymes namely endoglucanases (endocellulases), exoglucanases (cellobiohydrolases) and β -glucosidases (cellobiases). Enzymatic hydrolysis has a synergistic multistep catalyzing effect on cellulose. Endoglucanases attacks the amorphous region of cellulose structure and cleaves the internal bonds, exoglucanases (cellobiohydrolases) cleaves the terminal glycosidic bonds of both amorphous and crystalline regions of cellulose and forms disaccharides and tetrasaccharides. Further, these disaccharides and tetrasaccharides are hydrolyzed to glucose by action of β -glucosidases (cellobiases). The process yields high degree of nanocellulose with flexibility of milder operating conditions. However, the slow rate of hydrolysis and cost of enzyme limits its applicability on industrial scale [5].

C. Solid acid catalyst as an alternative for acid hydrolysis

Selective hydrolysis reaction of cellulose can be carried out by heterogeneous catalyze reaction through solid acid catalyst. It has many advantages over liquid sulfuric acid in terms of catalyst life time, activity, selectivity and reusability. Further, this catalyst reduces amount of environmental pollutants significantly. However, the key concern governs on feasibility of contact of catalytic acid sites to the β -1,4 glycosidic linkage as both remain in solid phases. Hence water has been chosen to act as a mass transfer medium. Further, generation of hydronium ions on surface of catalyst accelerates the hydrolysis process. Green acid catalyst includes iron based catalyst, heteropoly acid, ion exchange resin etc.

Lewis acid site of iron metal catalyst such as $FeCl_3$ and $Fe_2(SO_4)_3$ can act as catalyst for hydrolysis. Paramagnetic-based nanocatalysts such as suspension of Zn-Ca-Fe based catalyst hydrolyse the glycosidic bonds and presence of Fe enables physical separation of catalyst from the final product with help of an external magnetic field. Fe_3O_4 based nanoparticles are another alternative for solid acid based catalyst.

Heteropolycarboxylic acid possesses acidic strength similar to sulfuric acid and donates H^+ ions to oxygen atoms in the ether bonds of cellulose during hydrolysis action. Stability and high proton mobility make them a superior catalyst during hydrothermal hydrolysis. Catalyst recovery is done by converting the catalyst into

solid phase with help of organic solvent such as diethyl ether [4].

IV. DIFFERENT VARIANTS OF CELLULOSE NANOFIBRILS

The extracted CNF is physically obtained in different forms. Primarily CNFs are obtained in aqueous suspensions. However, drying of these highly viscous aqueous suspensions results in obtaining CNFs in powder form which has very little solid content. Further, drying of CNF is difficult as cellulose tends to get entangled. Aqueous suspensions of CNF's can be dried to obtain films. Hydrogels and aerogels are the other variants of CNF suspensions.

V. POST TREATMENT-SURFACE CHEMICAL MODIFICATION OF CNCs AND CNFs

Pretreatment enables reduction of energy demand during processing of nanocellulose while post treatment on the obtained product enables its compatibility with several polymer matrices with an aim to obtain value added products. Physical adsorption, molecular grafting, polymer grafting is some of the methods to induce surface functionalization on nanocellulose surface. The present section discusses about the objectives and basic principles of the several functionalization routes.

Physical adsorption comprises the use of surfactant for tuning the surface of nanocellulose. One such example is adsorption of cationic surfactant cetyltrimethylammonium bromide (CTAB) on surface of anionic CNFs obtained from TEMPO assisted route. The process induces hydrophobicity to the CNFs without altering the mechanical properties. Surface modification through polyelectrolyte solution also takes place in adsorption route. A pre oxidized nano cellulose substrate is useful for amidation coupling though the help of carbodiimide mediated reaction. Amidation of TEMPO mediated oxidized cellulose can result in formation of alkyne derivative or azide derivative. One set of alkyl and one set of azide derivative can be further reacted in click reaction to obtain unique functional properties on CNCs.

Hydrophobicity on cellulose surface has been usually achieved by esterification process involving acid anhydrides and acyl chlorides. Similarly, carbonylation i.e. reaction of isocyanates with hydroxyl group of cellulose imparts urethane linkage which also introduces hydrophobic nature to the CNFs. Addition of reactive derivative of fluorophores such as fluorescein isothiocyanate, rhodamine B isothiocyanate etc. on CNCs enables its applicability in the field of nanomedicine and pharmaceutical drugs.

Introduction of positive charge on nanocellulose is achieved through the etherification process by utilizing quaternary ammonium salts. In this method, alkali activated cellulose undergoes the cationization process to form a stable aqueous suspension.

Silylation of cellulose works as a coupling agent for composite fabrication in which organofunctional silane is attached with hydroxyl group of cellulose and other functional groups of silane gets attached to the polymer matrices.

In surface functionalization methods of CNCs, covalent attachment of long chain polymer takes place in

two approaches viz. “grafting from” and “grafting onto”. As the name suggests grafting onto approach is used for coupling of polymer molecules on the nanoparticle surface. However, steric hindrance induced by the polymer molecules and high working viscosities limits in achieving high grafting densities. The other feasible approach is mixing of activated CNCs with a monomer and initiator to initiate the polymerization process from the nanoparticle surface. A low degree of polymerization is achieved in this process [9-11].

VI. APPLICATION

CNFs when combined with various nanoparticles become an excellent choice of material for fabrication of composites. Surface functionalized CNF based membranes are heavily used in the field of water purification owing to its high surface area, non-toxicity, hydrophilicity and adsorption abilities. Modified CNF based templates are actually useful to adsorb heavy metals from the pollutant water. Another high prospectus area of nanocellulose is its usage in the field of biomedical engineering and drug delivery system. Further, nanocellulose is widely applicable for sensing humidity, gas, mechanoresponsive sensing etc. Miscellaneous application of nano cellulose includes template for inorganic particle synthesis, food packaging material, nano coating agent, automotive industry etc [4,5,12].

VII. SUMMARY AND CONCLUSION

This review provides the basic flow line for extraction of nanocellulose from lignocellulosic materials. In this process, the manuscript highlights the basic structure of cellulose and elaborates the impact of crystal and amorphous region of cellulose on its properties. Further, it has been identified that lignocellulosic materials are the prime sources for extraction of cellulose. Hence structure of lignocelluloses is highlighted to emphasize the need of pretreatment process required for cellulose extraction. The review briefly presents several industrial as well as research oriented pretreatment process. After isolating cellulose from non-cellulosic substances of lignocellulose, this review collates chemical methods and enzymatic hydrolysis techniques used in the process of converting cellulose to nanocellulose. The manuscript additionally provides different sources of nanocelluloses while describing the difference between CNCs and CNFs. Similarly, it also provides a summary of different physical forms of nanocellulose. Further, nanocellulose has a wide domain of application by enhancing its properties through surface functionalization. The surface hydroxyl groups of cellulose, which are reactive can be tailored to impart non-covalent or covalent bonding primarily for introduction of hydrophobicity and increase miscibility with several polymer systems.

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