REVIEW ARTICLE

Preparation and Application of Nanocellulose (NC): Review

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Now a day, cellulose nonmaterial's and its application advance extraordinary fascination in both industrial and academic research fields. This is owing to its special behaviors including advanced mechanical behaviors, amazing surface area, abundant hydroxyl groups for adjustment, and benign environmental properties. This review was focused on the study of recent preparation techniques of nanocellulose from lignocellulosic biomass and its fundamental applications in environmental and energy related areas. Mostly, the cellulose nanomaterial preparation techniques associated to ball milling are summarized. In addition to this, a perspective on its upcoming is specified. Again, this review will help the scientific community working on the effective preparation of cellulose nanomaterials from lignocellulosic biomass and its greatest conceivable applications in the upcoming day.

Introduction

Environmental pollution is defined as a progression in which any material presented into surroundings that adversely affects the expediency of assets. Generally, it can be classified into three namely water, air and land pollution. At present time, a serious environmental pollution throughout the world is triggered by the fast growth of industrial activities and human population in last few decades. Water is the most indispensible and significant constituent for all living things in the world. In the previous period, anthropogenic water mandate has augmented sevenfold because of the increased global population [**1-3**]. Water pollution, because of the elevated levels of several contaminants or pollutants such as, toxic heavy metal ions, inorganic anions, micro-pollutants, organic compounds such as dyes, phenols, pesticides, humic substances, detergents and other persistent organic pollutants, has been widely researched in different areas of the world in current periods [**4**]. Release of these toxic pollutants into the accepted water bodies has momentously affects the biological equilibrium and has instigated harmful effects on flora and fauna [**5**]. Numerous pollutants present are not only resistant against chemical or biological degradation, but also have extraordinary environmental movement and robust affinity for bioaccumulation in the food chain [**6**].

From the above stated contaminants, pollution because of toxic elements such as Pb(II), Hg(II), Cd(II), Pd (II), etc. are posturing a severe risk both for human beings and animals. The definitions of heavy metals are elements with an atomic density advanced than 6g cm^{-3}. Nevertheless, it is merely a loosely defined term, which is extensively documented and commonly applied to the metal elements related with contamination and poisonousness difficulties [**7**]. Substantial quantity of several poisonous metals are discharged into aquatic body by several kinds of industries, such as mining and smelting of minerals, the surface finishing industry, energy and fuel production, fertilizer and pesticide industry and subsequent application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, aerospace and atomic energy installation etc. [**8**]. Due to this reason, it is essential to remove pollutants from wastewater prior to its release into the normal environment.

Different conventional methods are utilized for eradicating several pollutant ions from wastewater. These are redox process, membrane separation, extraction of liquids, exchange of ions, electrochemical methods, coagulation, flotation, evaporation, hydroxide and sulfide precipitation, crystallization, ultrafiltration, and electrodialysis [**9-14**]. The listed approaches differ in their efficiency and economy consuming diverse eliminating representatives. So many researches have reported different physico-chemical treatment methods for water and wastewater treatment using different eliminating representatives [**15**]. These eliminating representatives can be from different sources such as organic or inorganic roots: activated carbons, metal oxides of nanomaterial's, and silica beads. Furthermore, they resulted from low-cost materials, i.e. the industrial by-products, agricultural wastes, biomass and polymeric materials such as organic polymeric resins, and macro-porous hyper cross-linked polymers. From all these purification methods, adsorption by means of activated carbon has been measured as one of the finest substitute usages for water and wastewater purification owing to its outstanding pollutant up take capacity with the absence of harmful by-products [**16-17**].

Though, activated carbon has big limitation for removing pollutants in large scale water purification of developing countries owing to its expensiveness and difficulty for reuse.

Thus, in the recent time there is the principal development of low cost and environmentally friendly materials such as, polymeric materials is gaining thrust over the entire world. Nanocellulose (NC) is a natural nanomaterial that can be prepared from lignocellulosic biomass and used as removing agents in place of activated carbon owing to its cost effective and simply regeneration through acid washing. With its nanometer size in diameter, NC consists of gorgeous properties such as high strength, excellent stiffness, and high surface area [**18-21**]. Moreover, with its structure, it encompasses an abundant of hydroxyl groups which are available for surface amendment. It can be applied in several areas, such as environmental, energy, water treatment, biomedical products, nanocomposite materials, textiles, and so on [**22-24**]. Currently, NC gets extraordinary fascination from research and an industry owing to the study of NC is not only about its preparation from biomass, but also the new environmentally friendly applications in numerous fields. The objective of this review is to show the recent trends in preparation methods of NC and its applications in wastewater treatment.

Lignocellulosic biomass

Lignocellulosic biomasses are plant based materials that contains the principal quantity of sustainable carbon containing substances and shows potential feedstock for the preparation of NC [**25,26**]. Especially, it is the largest resource for most natural fibers and can easily substitute the activated carbon due to its wonderful price efficient and environmentally sociable properties for wastewater decontamination [**27,28**]. Besides, the agricultural wastes and forest deposits are paramount important for recycle adsorbent or feedstock for fabrication of efficient materials for wastewater decontamination without the antagonism with both human and animal food chains [**29,30**].

The cell wall structure of lignocellulosic biomass mostly contains three kinds of polymers, such as, lignin, hemicellulose, and cellulose. Though, the composition and the levels of these three constituents are differed because of the variation in sorts, kinds, and foundation of lignocellulosic biomass [**31,32**]. Thus, approximately 10–25% and 20–35% by mass of dried out lignocellulosic biomass correspond to lignin and hemicelluloses, respectively [**33,34**] (**Fig. 1**).

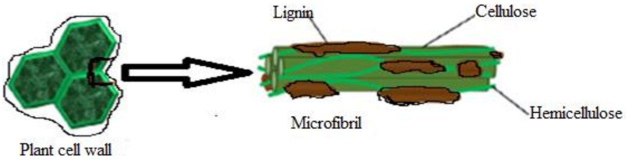

Fig. 1. Main structure of plant cell wall in lignocellulosic biomass which is consisted of lignin, hemicellulose, and cellulose.

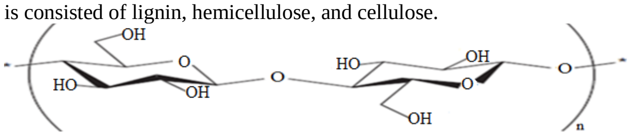

Fig. 2. Schematic representation for the structure of cellobiose.

Cellulose is the most important constituent in lignocellulosic biomass and mainly contained in the plant cell wall about 35–50% [**33,34**]. Cellulose is made of the linear homopolysaccharide β-1, 4-linked anhydro-D-glucose units through the replicating items of cellobiose (**Fig. 2**) [**35**]. The monomer of anhydroglucose unit contains three hydroxyl groups that form strong hydrogen bonding through the adjacent glucose unit within the same chains (intramolecular) and between the different chains (intermolecular) hydrogen bonding networks (**Fig. 3**) [**35**]. These networks are most powerful and strongly crammed in the more ordered components of cellulose fibrils which make it harder, strong, fibrous, and unable to dissolve by water and most organic solvents in plant cell wall [**36-38**]. In the cellulose, an ample orientation of glucose molecules and hydrogen bonding networks is possible, due to the presence of different allomorphs of cellulose [**35**]. Different cellulose allomorphs are varied due to the variation in source materials and different techniques implemented. These allomorphs are classified into four types such as, cellulose type I, II, III, and IV [**36-38**]. Cellulose type I is called the universal allomorph of cellulose in nature with the similar wadding of hydrogen-bonding arrangement. If one can chemically dissolve cellulose type I in acid or alkaline solution, then it is possible to find cellulose type II with anti-similar wadding of hydrogen-bonding arrangement. Through treatment of cellulose type I or II with ammonia, cellulose type III can be prepared. Cellulose type IV can be prepared by the heat treatment of cellulose type III at 260 ^{0}C in glycerol [**38**]. Thus, all these is widely used natural sources for the preparation of carbon-containing species, useful chemicals, textiles, papers, and etc. due to the presence of large number of carbons, hydroxyl groups and monomers of glucose [**39,40**].

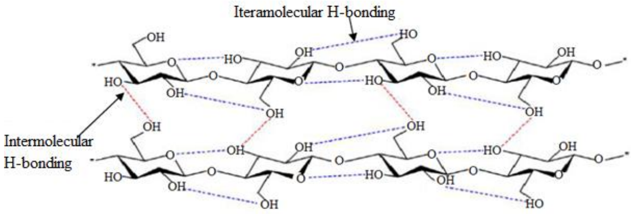

Fig. 3. Intramolecularand intermolecular hydrogen bonding networks in cellulose structure.

Nanocellulose

The term nanocellulose is substance in the nanometer range (1-100 nm in diameter) and made from lignocellulosic biomass. It is easily decomposable or biodegradable nanoparticles with less weight, very less density (around 1.6 g/cm^3) and excellent strength. It has different mechanical properties such as, high stiffness up to 220 GPa of elastic modulus relatively much higher than Kevlar fiber, outstanding tensile strength up to 10 GPa which is superior than cast iron and as well as its ratio of strength to weight is 8 times elevated than stainless steel. In addition to this, it is much transparent and having high reactive sites of hydroxyl groups suitable to functionalize the different surfaces with anions or cations [**41,42**].

The preparation of nanocellulose can be carried out using different lignocellulosic biomasses as source materials [43] through mechanical, chemical or enzymatic techniques. Both the bulk and smaller particle structure of cellulose contains amorphous and crystalline phases. The amorphous phase of cellulosic materials is easily broken by mechanical, chemical or enzymatic means, while, it is moderately tricky for the breakage of nanostructured crystalline phase of cellulose due to the presence of massive hydrogen force. Preparation of cellulose nanoparticles from its source includes two major steps viz. pretreatment and removal of amorphous phase by suitable techniques [**44**]. Before mechanical, chemical or enzymatic action, pretreatments such as alkali treatment and bleaching are required in order to remove certain amount of lignin, hemicellulose, wax and oils which envelop on the outside shell of the particle cell wall. The native cellulose structures are depolymerised and the outside parts of cellulose microfibrils are defibrillated through alkali treatment. Next to this, bleaching process is necessary to remove the cementing material totally from the particles [**45**]. Here, one can understand the nano dimensions, quality and yield of the prepared particles would depend on source of lignocellulosic biomass when same preparation techniques are applied.

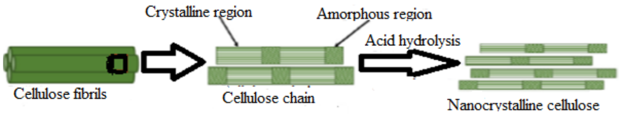

Fig. 4. Schematic of nanocrystalline cellulose which can be extracted from cellulose chains using acid hydrolyzed amorphous region and left only crystalline region.

The three main types of cellulose are; cellulose nanocrystalline (CNCs), cellulose nanofibrils (CNFs), and bacterial nanocellulose (BNC). No matter how, all types are alike in chemical composition, they vary in morphology, particle size, crystallinity and some properties, because of differences in the source materials and preparation techniques [**38**]. Cellulose nanocrystals (CNCs), called nanocrystal of cellulose, or cellulose nanowhiskers, are cellulose nanoparticles with lofty strength, usually prepared from cellulose particles by acid hydrolysis [**42**]. The resulted materials have short-rod-like shape or whisker shape with the diameter of 2–20 nm and the length of 100–500 nm. In addition to this, it consists 100% of cellulose chemical components mostly in crystalline parts (outstanding crystallinity about 54–88%) [**38**]. **Fig. 4** indicates the representation of CNCs that is prepared from cellulose particles by acid hydrolysis. Through acid hydrolysis the amorphous regions are easily hydrolyzed and removed, but the crystalline regions are not removed [**46**]. From this point of view one can conclude that, it is possible to prepare CNC that has high crystallinity with a short-rod shape using this preparation technique. Through mechanical techniques, CNF is prepared from cellulose particles which is long, flexible, and entangled materials. It has long fibril shapes and the diameter of 1–100 nm and the length of 500–2000 nm [**47**]. Also, it consists 100% of cellulose chemical components with both of crystalline and amorphous parts [**41**]. **Fig. 5** indicates the representation of nanofibrillated cellulose which can be prepared from cellulose fibers by the by mechanical techniques. Cellulose nanofibers (CNFs) have longer length with high aspect ratio (length to diameter), high surface area, and large number of hydroxyl groups which is easily accessible for surface modification relative to CNCs [**38**].

Nanocellulose can be categorized into BNCs which is different from CNC and CNF. The preparation of CNCs and CNFs can possible from lignocellulosic biomass (top-down process) but, BNCs is prepared from bottom-up process. Therefore, BNCs are always referred to as pure without any non-cellulosic components. They have the same chemical compositions as other two kinds of nanocelluloses. They are in the form of twisting ribbons with 20–100 nm in the average diameters and micrometer lengths with large surface area per unit [**47**].

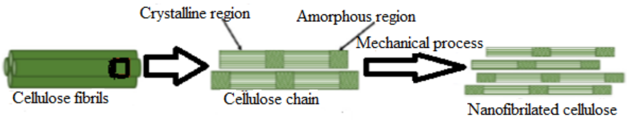

Fig. 5. Schematic of nanofibrillated cellulose which can be extracted from cellulose chains using mechanical process to cleavage the fiber into nanometer size in diameter.

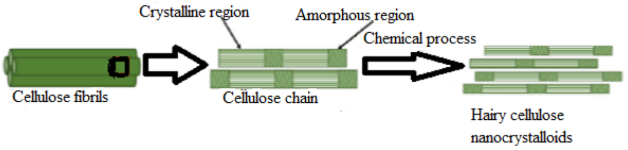

Fig. 6. Schematic of hairy cellulose nanocrystalloids which can be extracted from cellulose chains by chemical treatment.

Mechanisms of water purification using nanocellulose

The use of cellulose nanomaterials for water decontamination has grown to be a charmingstudyarea in the current existence. At the nano-scale level, resources are characterized by special physical, chemical, and biological properties relative to their bigger size species. The pollutant uptake capacity of conventional adsorbents is usually inadequate by their surface area or available binding places, the absence of selectivity and the very slow rates. Nano-cellulose based adsorbents give important enhancement with their tremendously high specific exterior areas related with binding sites and short intraparticle diffusion distance providing to rapid rates [**48**].

Adsorption is one pollutant removing technique from wastewater by using nanocellulose and defined as a process adsorbate or pollutants accumulates on the adsorbent surface either chemically or physically. The most important factors affecting the adsorption process are the particle size of adsorbent, affinity of the solute for the adsorbent, surface area of adsorbent, degree of ionization of the adsorbate molecule (more highly ionized molecules are adsorbed to a smaller extent than neutral molecules), solution pH etc. Optimizing these factors will enhance the pollutants uptake capacity. Therefore, this is happening a relationship exists between the concentration of the species in solution and the concentration of the same species in the adsorbed state i.e. equilibrium situation. The number of adsorbed pollutants is calculated by the difference of the original and equilibrium quantity of pollutants in solution divided by the weight of the adsorbent. The adsorbate in the glassware is calculated from mass balance as follow:

$$m(q-qe)=(Co-Ce)v \qquad (1)$$

From which a relationship between value of C and the corresponding equilibrium value of q can be established. To determine equilibrium relationship, $q_o = 0$,

$$qe=\frac{v}{m}(Co-Ce) \qquad (2)$$

Where, **v** is the volume of liquid, m is the mass of adsorbent used, Co is the initial, and Ce is the adsorbate residual concentration in solution.

During the adsorption process, dissolved substances are passed into the permeable adsorbent constituent part by dissemination and are then trapped onto the surface of the adsorbent. Both chemisorption and physisorption interaction is possible during adsorption process. In chemisorptions, the adsorbatebinds with the surface to form a covalent or an ionic bond results in bonding energies of >80 kJ/mol. In physisorptions, there is happen a rapid process caused by nonspecific binding mechanisms such as van der Waals forces and results in bonding energies of 4 - 40 kJ/mol. Generally, physical adsorption is less specific for which compounds adsorbed to surface sites, has weaker forces and energies of bonding, operates over longer distances (multiple layers) and is more reversible [**49**].

In contrast to the adsorption of organic adsorbates from water (polar solvent) onto a nonpolar adsorbent (carbon based materials), where van derwaals forces are predominating, adsorption of ionic species (e.g., metal ions) onto nanocellulose surfaces is mostly driven by electrostatic attraction, which is highly dependent on solution pH and ionic strength because of the charge differences. The affinity of the adsorbate for an adsorbent is quantified using adsorption isotherms, which are used to describe the amount of adsorbate that can be adsorbed onto an adsorbent at equilibrium and are usually a function of the liquid phase concentration. To develop isotherms, a known quantity of adsorbate in a fixed volume of liquid is exposed to various dosages of adsorbent.

Here, one can consider the significant differentiation between adsorption of a solitary and of multiple compounds. In the first case, the dissimilar adsorbates are competing for binding places and the adsorption equilibrium as well as the isotherm can be significantly dissimilar than without antagonism. In the second situation, the initial concentration of the target adsorbate influences the consequential isotherm. For the mathematical description of the adsorption equilibrium one can consider the existence of different models, differing in complexity and in the number of parameters. Mostly, for practical importance the two main parametric isotherms (Langmuir isotherm and Freundlich isotherm) are formulated [**50**].

The Langmuir isotherm is important for binding of a solute from a liquid solution as monolayer adsorption on a surface containing a fixed number of similar sites. This model describes the equilibrium between the adsorbent surface and adsorbate as a reversible chemical equilibrium between substances. It assumes homogeneous energies of binding onto the surface of the adsorbent without interaction of adsorbate in the plane of the surface where adsorbate molecules can be chemically bound. Its equation assumes that uniform arrangement of the adsorbent surface, i.e. all binding sites are energetically identical. Due to this reasons, the Langmuir equation is in most situations only relevant for small level ranges. Equilibrium parameter (R_L) indicates the isotherm shape and whether the binding is possible or not possible.

The Langmuir nonlinear equation is commonly expressed as follows (Langmuir 1918):

$$qe=\frac{Q_oCe}{1+bCe} \qquad (3)$$

To derive the model parameters Q_o and b, equation 3 can be linearized. The linear Langmuir isotherm allows the calculation of adsorption capacities and is equated by the following equation.

$$\frac{Ce}{qe}=\frac{1}{bCo}+\frac{Ce}{Qo} \qquad (4)$$

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by:

$$RL=\frac{1}{1+bCe} \qquad (5)$$

For all the above equation (1-5),C_o is the initial adsorbate concentration in solution (mg/L), C_e is the adsorbate residual concentration in solution, $q_o$is the initial amount of adsorbate per unit mass of adsorbent (mg/g), m is mass of adsorbent (g) and v is the volume of liquid, q_e is milligrams of adsorbate accumulated per gram of the adsorbent material, Q_o is the maximum uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates.

Table 1. Type of isotherm for various R_L.

R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L=0$	irreversible

The second important model is Freundlich isotherm model and can be derived assuming a logarithmic decrease in the enthalpy of binding with the raise in the portion of engaged places. This isotherm is generally improved to describe adsorption in aqueous solutions than the Langmuir isotherm. This model is commonly given by the non-linear equation [**49**]:

$$qe = KfC_n^{\frac{1}{n}} \tag{6}$$

K_f represented the adsorption coefficient and tells the quantity of adsorbate binded onto adsorbent surface for unit equilibrium concentration and known as a constant for the system related to the bonding energy. 1/n is represents an empirical constant associated to the extent of the adsorption driving force onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The linearized form of the Freundlich equation that determines both K_f and n were given by [**51**]:

$$\log qe = \log Kf + \frac{1}{n}\log Ce \tag{7}$$

Next to the adsorption isotherms, the adsorption kinetics gives the statement of adsorption rates and significant information for scheming and modeling of the progressions. The important application of the pollutant binding process demands improvement of cheap, easily available and plentiful adsorbents of known kinetic parameters and sorption characteristics. Until now, numerous kinetic models (pseudo first- and second-order equations, intra-particle diffusion and Elovich equations) are implemented to construe the time dependent experimental data and inspect the controlling mechanism of pollutant binding process [**52**]. The Pseudo-first order model [**53**] is given as:

$$\log(qe - qt) = \log Qe - \frac{K1t}{2.303} \tag{8}$$

The pseudo-second-order kinetic model equation [**54**] is given as,

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{t}{qe} \tag{9}$$

Also, the spontaneity of the adsorption processes was easily determined by obtaining information from thermodynamics concept. Therefore, one can understand the concept of standards Gibb's free energy change (ΔG^0) to determine a given process whether spontaneous or non-spontaneous. If the value of ΔG^0 is negative, then the reactions occur spontaneously at a given temperature. The thermodynamic parameters such as change in standard free energy ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) can be calculated by using the following equation [**52**]:

$$\Delta G^0 = -nRTlnKc \tag{10}$$

$$InK_c = -\Delta H^0/RT + \Delta S^0/R \tag{11}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{12}$$

where R (8.314 J/molK) is the gas constant, T (K) is the absolute temperature and K_c is the standard thermodynamic equilibrium constant defined by q_e/C_e. By plotting the graph of lnK_c versus T^{-1}, the value of $\Delta H^0$and ΔS^0 can be estimated from the slopes and intercept, respectively.

Finally, the important mechanism is regeneration of used adsorbents by re-obtaining the used adsorbents through acid washing. If adsorption is thought of as surface complexation reaction a high concentration of H^+ ions shifts the equilibrium so that less adsorbate (pollutants) is bound to the surface. In addition to this, the surface acid/base reaction is shifted more towards positively charged species, which hinders adsorption of cations such as metal ions. As a result, a pH decreases due to the use of HCl, shifts the adsorption equilibrium and can result in desorption of the adsorbed solute (metal ions). If the adsorption capacity can be regained in this process, the adsorbent was regenerated. In many studies, hydrochloric acid (HCl) solution has been shown as suitable regenerant for cellulose based adsorbents as well as hybrid anion exchange resins. The pollutants desorb ability was defined as:

$$\text{Percent of desorption } (\%) = \frac{desorbed}{adsorbed} * 100\%\ldots \tag{13}$$

where, Desorbed: the concentration of the metal ions after the desorption process Adsorbed: (C_o – C_e) for each recovery process.

Preparation of nanocellulose from lignocellulosic biomass

Because of the significant interesting properties of nanocellulose and option for the prospect functions, the research on nanocellulose preparation from lignocellulosic biomass is extremely important, particularly for the preparation from the agricultural wastes. **Fig. 7** indicates the representation of nanocellulose preparation from lignocellulosic biomass which contains of two major steps. Initially, the non-cellulosic components, such as lignin, hemicellulose, and other compounds, are detached by the pretreatment. Then, nanocellulose is prepared from cellulose particles by different preparation techniques [**55,56**].

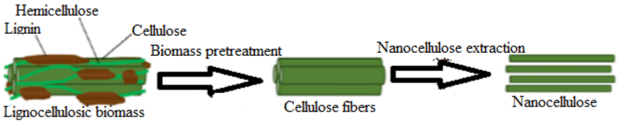

Fig. 7. Schematic of nanocellulose extraction from lignocellulosic biomass.

Biomass pretreatment

Currently, the agricultural residues are significant for the valuable resource for nanocellulose preparation. Using agricultural wastes is not initiated only due to the highly available in nature, but also using it can advance the importance from non-valuable wastes to very significant important profits of nanocellulose [**57**]. Additionally, the important of using agricultural residues are to make the environment cleaner. As stated previously in the above, lignocellulosic biomass contains of cellulose and non-cellulosic species including lignin, hemicellulose, and etc. These non-cellulosic components are removed by the pre-treating the lignocellulosic biomass both alkaline and bleaching process and remaining with cellulosic materials for further extraction of nanocellulose [**55,56**].

Acidchlorite treatment and alkaline treatment are the two important techniques for biomass pretreatment. The first one are termed as the delignification process, or bleaching process, which is mostly used in pulp industries [**58**]. This processes are carried out in order to remove most of non-cellulosic components by the combination of distilled water, sodium chlorite, and acetic acid stirring with lignocellulosic biomass at 70–80^{O}C for 4–12 hrs (C (Johar *et al.* 2011; Santos *et al.* 2013). The acetic acid and sodium chlorite are mixed at interval time for managing the pH value. Next, the solution is reserved inspiring overnight, followed by cleaning with distilled water till the pH of 7. The resulted hard yields are gathered and dried in oven at 50^{O}C, the yield is holocellulose, mostly including hemicellulose and cellulose in the fibers. The total deduction of lignin and any other impurities are confirmed by the formation of white color fiber holocellulose [**59**].

The alkaline treatment is the use of strong bases for avoiding the amorphous materials of hemicellulose and the not removed lignin. Sodium hydroxide (4–20 wt%) is the mostly used alkaline, which is constantly mixed through holocellulose for 1–5 hrs. Then, the resulted solid yields are cleaned by distilled water till pH of 7 and lastly dried in an oven at 50^{O}C. The resulted yields from this process are mostly in the form of cellulose, and the rest non-cellulosic components have been uninvolved. Currently, numerous researchers used these biomass pretreatment techniques to remove non-cellulosic materials from agriculture residues [**59**]. For example, Johar *et al.* [**59**] used this technique for pretreatment of rice husks with alkaline followed by a bleaching process. From these reports it is possible to conclude that the content of cellulose was enhanced from 35 wt% in not treated rice husks to 96 wt% in yields after pretreatments.

Preparation of nanocellulose

There are suitable techniques for the preparation of nanocellulose from lignocellulosic biomass. Different preparation techniques used leads in the differences in types and characteristics of the resulted cellulose nanomaterials [**60**]. In this sub portion, the main preparation techniques are grouped into three: namely, acid hydrolysis, enzymatic hydrolysis and mechanical process.

Acid hydrolysis is one of the principal procedures for the synthesis of cellulose nanomaterials from lignocellulosic biomass. Because of the combination of crystalline and amorphous parts in cellulose chains, the amorphous parts can be simply hydrolyzed by acid and the crystalline regions are not hydrolyzed [**38**]. The most importantly used acid here for hydrolysis are sulfuric acid. The significant of this acid is not only to isolate CNC, but also to make the cellulose nanomaterials dispersed as a stable colloid system due to the esterification process of hydroxyl group by sulfate ions [**61**]. The major monitoring parameters that influence the characteristics of the resulted nanocellulose are reaction time, temperature, acid levels and cleaning process [**60**]. The cleaning process is usually done by adding water next by centrifugation till the pH of 7 [**59**]. An additional technique for cleaning the resulted yields is using the alkaline such as sodium hydroxide for neutralization process [**62**]. For instance, Maiti *et al.* [**63**] prepared cellulose nanomaterials from three different kinds of biomass by acid hydrolysis with 47% sulfuric acid. After the end of the reaction, the acid is completely removed by cleaning it with deionized water and centrifuged and after that, 0.5 N of sodium hydroxide is added for neutralizing the suspension, followed by cleaning another time with distilled water.

A technique in which enzymes is used for digesting or modifying cellulose fibers are known as enzymatic hydrolysis [**40**]. In general, this technique is called biological treatment and enzyme can be used as modifier. Generally, it is performed in mild conditions; though, lengthy time of action is required. To overcome such difficulty, the enzymatic hydrolysis is all the time integrated with another technique. Moniruzzaman and Ono [**64**] reported the preparation of cellulose fibers from wood chips by pretreatment with ionic liquid for increasing the available surface area, next by enzymatic hydrolysis with lactase. The resulted cellulose nanomaterials indicated 100% crystallinity and thermal stability than the native wood fibers.

The extraction of cellulose nanomaterials using mechanical method to break the cellulose fibers in longitudinal axis is known as mechanical process [**65**]. The mainly implemented mechanical technique includes high pressure homogenization, ultrasonication, and ball milling techniques.

High pressure homogenization (HPH) is for all time carried out by introducing cellulose slurry into a container with elevated pressure and rapid rates [**65**]. The collision force and shave force in liquid are generated to break cellulose micro fibrils into nanometer size in diameter. For example, Li *et al.* [**34**] extracted cellulose nanomaterials from sugarcane bagasse by high pressure homogenization with a diameter of 10–20 nm with lower crystallinity than the original cellulose [**34**]. The less degree of crystallinity formed because of the intermolecular and intra-molecular hydrogen forces of cellulose molecules were conked out throughout the high pressure homogenized process.

The other mechanical technique used to extract cellulose nanomaterials is called ball milling. Because of the presence of centrifugal force from the rotating jar, the shave forces are generated within balls and between balls and the surface of jar [**66-68**]. Due to this reason, the cellulose fibrils are splintered to the nanometer size in diameter. Nevertheless, the major short coming of this process is the use of high energy during the process. In order to overcome this problem, this process is generally combined with other pretreatment techniques for lowering energy consumption [**69**].

Bya variety of laboratory scale studies in order to build up innovative preparation techniques, a number of methods have previously been functional in pilot scale and at industrial level. The extraction of cellulose nanomaterials was initially started in a pilot plant scale in 2011 [**70**]. Currently, cellulose nanomaterials preparation is increasing in manufacturing scale which is extensively broaden mostly in Canada, USA, Europe, and Asia such as China, Japan, Iran, and India [**29**]. The preparation techniques recently accessible in industries are largely those predictable techniques such as sulfuric acid hydrolysis for preparation of nanocrystalline cellulose and mechanical treatment for preparation of nanofibrillated cellulose [**70**]. This is due to they are the successful preparation methods in lab scale which have been created for numerous decades before to introduction in industry scale. No matter how, the chief economic barrier of the recent cellulose nanomaterials preparation is the many-step progression, including high cost of chemicals, high cost of preparation and preservation of apparatus operated in acidic medias, hard acid wastewater purification for the processes such as acid hydrolysis technique, and high energy consumption for the mechanical process. Due to these reasons, the improved alternative of preparation technique for the scale up is the solitary step process which can frankly prepare cellulose nanomaterials from lignocellulosic biomass wastes.

It is worth noting that ball milling technique becomes an elevated probable for additional advance in preparation and function of cellulose nanomaterials. It has been extensively intended for grinding materials and particle alteration since 1990s. The most important apparatus of ball milling machine consist of milling balls (or grinding media) with different sizes enclosed in the milling jar (or milling beaker, milling vessel). Recently, there are different kinds of ball millers extensively used in industry and laboratory scale such as, planetary ball mill, mixer ball mill, and vibration ball mill [**71**]. From all of these, the planetary ball mill is regularly used for disintegration of cellulose.

Fig. 8 indicates the planetary ball milling technique which is a mechanical method created from the clash between balls to balls and the abrasion of balls to the wall of milling jar which moved in revolving [**72-74**]. The collision from the moving balls and jar led to the grinding of materials because of the abrasion effects. This process results the smaller size with large surface areas and many active sites of nanocellulose. No matter how, there are a variety of variable factors which exaggerated the characteristics of ball milled yields such as, the number and size of balls, the milling speed, the state of milling (dry or wet state), the weight ratio between balls and materials, and milling time [**74**].

For the effective preparation of cellulose nanomaterials ball milling technique was also used for the pretreatment of cellulose before to acid hydrolysis. The effect of ball milling on cellulose paper with various milling circumstances before to the sulfuric acid hydrolysis in a less level situation was studied [**29**]. It is resulted that the pretreatment by ball milling leads in the smaller size of nanocellulose in diameter that be capable of promoting acid hydrolysis method in mild circumstances.

Table 2 indicates the ball milling techniques which was directly used for the preparation of nanocellulose in the early 2010s. Baheti *et al.* [**75**] reported the ball milling of jute fiber residues for the preparation of cellulose nanomaterials. They pretreated the Jute fiber residues by suitable chemicals for removal of lignin and hemicellulose before disintegration by the ball milling. The association of dry condition and wet condition (milling with deionized water) of the ball milling was also carried out. Actual widespread particle size dissemination was perceived by dry milling condition compared to wet milling condition. This is because, penetrating of material to the surface of vessel next to convinced period of milling condition. This is owing to the dominant role played by surface forces in dry state leading to the confession of material on the surface of milling media and aggregation but these phenomena was not possible in wet condition and resulted narrow particle distribution. Therefore, ball milling in wet condition is preferable for the preparation of nanocellulose from lignocellulosic biomass.

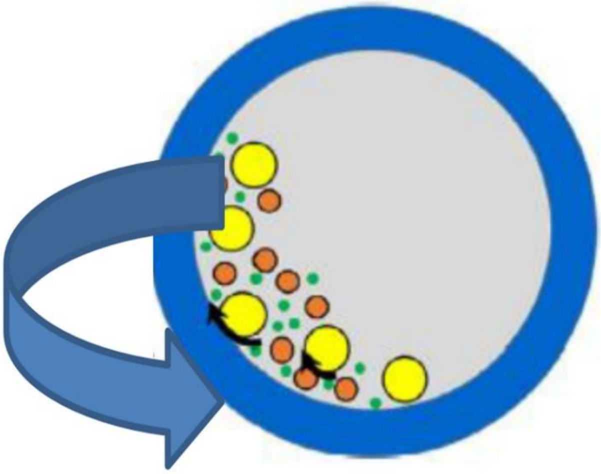

Table 2. Progress of nanocellulose extraction by ball milling.

Year	Raw material	State	Milling condition	Size of nanocellulose	Reference
2012	Jute fiber wastes	Wet (deionized water)	3 h, 850 rpm, 10:1 of BMR	<500 nm in diameter	[75]
2015	Northern bleached softwood pulp kraft	Wet (10 wt% in water)	1.5 h, 0.4–0.6 mm of ball diameters, 40:1 of BMR	100 nm in diameter	[76]
2015	Australian native grass (Triodiapungens)	Wet (1 %w/v aqueous dispersion) 30 min, 1000 rpm	0.4 mm of ball diameters 8.7 ± 4.8 nm in diameter	with few microns in length	[77]
2016	Sugarcane bagasse	Wet (50 mL of deionized water)	1 h, 0.5 mm of ball diameters, 80:1 of BMR	240 ± 12 nm in diameter with 10 mm in length	[78]
2016	Kenaf fibers and wheat straw	Wet (10 mL of 80% ethanol/ water mixture)	2 h, 12.7 mm of ball diameters	8–100 nm in range	[79]
2017	Cellulose powder	Wet (BMIMCl and distilled water)	2 h, 400 rpm, 12:1 of BMR	10–25 nm in diameter and micrometer scale in length	[29]

BMR = Weight ratio of balls to materials

Fig. 8. Schematic representation of planetary ball milling.

From the above **Table 2,** the inferences are the addition of water or liquid during the ball milling can guard it from the agglomeration of resources within the instruments and leads in the narrow particle size distribution in nanometer scale. Though, with this initial study of using ball milling for preparation of cellulose nanomaterials, the resulted size was till as large as around 500 nm of diameter which desires to additional regulation of milling conditions for reducing the size in nanometer range. Zhang *et al.* [**76**] studied the ball milling conditions, in detail which could influence the preparation products of cellulose nanomaterials rather than amorphous particulates. As raw material they used Northern bleached softwood kraft and the dry pulp was soaked in 10 wt% water overnight priorto ball milling at various situations. The results showed that the size of milling balls is significant for monitoring the nanocellulose yields. In addition to this, ball milling time and weight ratio of ball to material were also significant for monitoring the clash between balls and raw materials for the production of fibrous morphology within nanometer range.

For the preparation of cellulose nanomaterials using ball milling technique, milling in a wet condition is appropriate to preserve the fibrous state and avoid from the disintegration to unstructured state. Phanthong *et al.* [**29**] firstly studied the preparation of cellulose nanomaterials by using the combination technique of ball milling with ionic fluid. No matter how, the dissolution of cellulosic materials by ionic fluid requires a great temperature or under ultra-sonication condition. Using ball milling technique in wet condition at room temperature was effectively stimulated the dissolution in ionic fluid with a size decrease of nanoparticle. The particle size distribution of cellulose powder after stirring with BMIMCl (1- butyl-3-methylimidazolium chloride) was given in the **Table 2**. And the size of resulted cellulose nanomaterials was found to be in the range of 10–25 nm in diameter and a few micrometers in length.

In mechano-chemical techniques, ball milling is the mostly applicable method. Mechano-chemistry syndicates the mechanical and chemical methods in combination. For instance, the chemical conversion of the fiber surface can be appreciated by the mechanical force after ball milling technique [**80**]. Liimatainen *et al.* [**81**] extracted dialdehyde cellulose using ball milling of kraft wood pulp using sodium periodate as a good oxidizing agent. This process was conducted at the speed of 3500 rpm at nearly 27^{o}C for the range of 5–60 min. the results show that only 5 min of ball milling process can found in the reduction of the microfiber size of kraft wood pulp to a few hundred of nanometers in width with the length of below 50 mm. Furthermore, an increased time of ball milling process led to the enhancing of available surface sites for the obtained cellulose nanomaterials, which is advantageous for the surface modification using oxidizing agent. Sirvio *et al.* [**82**] extracted the dialdehyde cellulose using mechano-chemistry, in which bleached birch was milled by sodium periodate as oxidizing mediator and throughionic liquid (LiCl and $CaCl_2$) as initiators. In this process, the milling was accompanied at room temperature with the speed of 2000 rpm and the time of 180 min. the resulted dialdehyde cellulose fiber with an extraordinary aspect ratio can be resulted in the beginning of 15 min of milling time. Furthermore, the addition of ionic liquids can increase the redox process during the ball milling.

Application of nanocellulose

Nanocellulose is very important for the applications in many fields such as environmental and energy related areas due to its excellent physical, mechanical and chemical properties and biodegradable nature.

Environmental

In the area of environment, nanocellulose is mostly used as adsorbent in wastewater treatment due to it has a high surface-to-mass (or volume) ratio which is the basic property of adsorbent, large contact area enhances physical adsorption ability. Besides, it can be chemically modified for increasing pollutant-binding capability by hosting new functional groups [**83**].

Cellulose nanomaterials based adsorbents have the probable to successfully eradicate poisonous components from the aqueous media. For instance, a composite adsorbent based on poly(itaconicacid)-poly (methacrylicacid)-grafted cellulose nanocellulose for the elimination of Uranium ions from the aqueous media was studied [**9**]. The binding ability of resultant adsorbents becomes high when we increase the carboxylic group concentration on the surface of the adsorbents due to the increase in surface area of the adsorbents. Sushma *et al.* [**84**] reported a composite adsorbent based on cellulose-nano-silver particles embedded pebbles for the friendly economic use and reusable method for operative elimination of pollutants such as dyes, heavy metals and microbes from the aqueous media. In the composite adsorbent, silver Nano embedded pebbles eradicate microbes, whereas, Nano cellulose eliminates the dyes and heavy metal. Also the treatment of water and polluted air was carried out by using the photo catalytically active and suitable composite adsorbents of bacterial nanocellulos and TiO_2. Zhang et al. studied an ultra-light, flexible, hydrophobic as well as oleophillic sponge based on nanocellulose and methyltrimethoxysilane sols synthesized by freeze drying. This adsorbent can bind a numerous number of poisonous organic solvents and oils with capabilities up to 100 times of its own weight, based on the solvent and oil characteristics. Silylated-nanocellulose sponges has excellent flexibility, and shape stability in oil and solvent [**76**].

Due to the outstanding specific surface areas and the presence very large number of reactive groups, high binding capacity may be resulted with various types of modified cellulose nanomaterials. Nanotechnology reinforcement of pristine cellulose considerably increased metal elimination competence in comparison with rice straw and cellulose fibers. Nanocellulose particles were extracted using the physico-chemical treatment of rice straw, and were characterized and explored for the removal of some poisonous metals from wastewater [85]. Cellulose nanofibers were resulted to have long rod-like elongated nanofibrillated morphology, with an average grain size of 6 nm. The extracted cellulose nanofibers in batch experiments indicated an elimination competence of 9.7 mg/g Cd (II), 9.4 mg/g Pb(II), and 8.6 mg/g Ni (II) ions. The redevelopment studies indicated that nanocellulose fibers could be consecutively used for up to three rounds of reuse.

Due to the presence of extraordinary surface area nanocellulose based adsorbents are ready for surface modification and afford an interesting substitution to the conventional adsorbents such as, activated carbon, ion exchange resins, or zeolite. In the area of water purification, the potential use of surface modified nanocellulose was reported by numerous current journals that indicated the opportunity to formulate adsorbents based on modified nanocellulose for removing both heavy metal ions and organic pollutants. This surface modification process, was carried out through the addition of particular modifiers such as hydroxyapatite [**86**], amine [**87**] and xanthate [**88**] on the surface of cellulose.

Energy

Currently, lignocellulosic biomass has expected substantial attention as a superior material, and due to its greater mechanical properties made from the exceptional crystal structure, it has been used in different emerging high-tech areas such as bioengineering, flexible electronics, and clean energy [**89**]. In addition to this, cellulose acts as an environmentally friendly renewable material; especially CNFs have enhanced merits in energy related application. Relative to plastic substrates, nanopaper shows advanced thermal stability and coefficient of thermal expansion (28.5 ppm/K). CNFs link with each other and simply produce porous structures that enable ion and electron transportation [**90**]. This material has exceptional geometries and they are extremely environmentally friendly and cost effective [**91**] and shows tremendous flexibilities and mechanical stabilities and are implemented as structural supports for electronic devices [**92**]. Also, this green material can effectively promote potential applications as lateral heat spreaders in flexible energy storage devices and the thermal conductivity may enable the applications in thermal management.

Therefore, these materials are significantly used for the fabrication of energy devices such as flexible electronics, super-capacitors, solar cells, lithium-ion batteries, etc. [**93-97**].

Flexible electronics

Currently, the new consumer devices was rapidly shifted from rigid counterparts to flexible electronics due to the substantial importance of the flexible electronics considered more lightweight, mechanically friendly, and long aged compared to conventional electronics [**98**]. Mainly, flexible electronics have been confirmed, as competitive device performance relative to recent opposite electronics. Here, nanocellulose-based films are appealing green resources for flexible electronics due to their many advantages, permitting current electronics to transfer toward high performance and manifold beneficiary applications, in addition to being more portable, disposable, low cost, and biodegradable. Numerous electronics with nanocellulose-based resources have been advanced currently, such as, solar cells [**99**], touch screens [**100**], etc. Due to the inadequate time and space, though, the reviewer was only discussed the emerging applications of nanocellulose-based film in flexible electronics.

Super-capacitors

Super-capacitors (SCs), have fascinated important consideration amongst investigators throughout the last few decades because of their distinctive developments: high energy density, fast charging/discharging rate, high power density, good fundability and safe operation [**101**].

Energy storage of SCs can be divided into two classes giving to the charging/discharging contrivances - electrochemical double-layer capacitors (EDLCs) and pseudo capacitors [**102**]. In EDLCs, energy is deposited by ions adsorbing at the boundaries of the electrode [**103**] and therefore, its ability performance is controlled by accessible surface area and conductivity of electrode. As mentioned above, a huge specific surface area is promising for EDLC-based energy storage subsequently it delivers additional space for electrolyte ions adsorption. Extremely permeable and mechanically strong materials, such as aerogels and films, can be prepared when NC is intertwined [**104**]. This porous structure indicates pronounced probable as a substrate for flexible SCs by packing with carbon conductive materials, like CNTs [**105**] and, therefore, NCs have been extensively used in the flexible solid-state SCs.

Lithium-ion batteries

According to review reported by Zhang, *et al.*, [**90**], the separator of LIBs synthesized from CNFs can meaningfully decreases short-circuit found inside the battery. The CNF film has uniform porous structure that makes its thermal stability and wettability considerably improved than PP/PE/PP composite. The conventional electrode material is based on a metal foil, and the external part is coated with an active material, conductive agent, binder, etc. Due to the huge contact thermal resistance between the metal foil and the active material, the thermal conductivity is not good, and weak interfacial bonding may even reduce active material to fall off from the surface of the current collector, causing weakening of the cycle achievement of the LIBs [**106**]. The characteristics of safety, reliability and flexible geometry design electrolyte were prepared from LIBs with gel polymer. A lower conductivity of ion electrolyte and poor mechanical properties resulted from the conventional gel polymer electrolyte synthesized by solvent casting method was due to a mass of plasticizer is added during the preparation. The interior of CNF hydrogel is three-dimensional network structure composed of nanofibrils intersection. Therefore, the CNF hydrogel could exhibit good mechanical performance and high moisture content of more than 95 % [**107**].

Conclusions and future predictions

No matter how cellulose nanomaterials have various high properties and major accessibility in nature, the preparation of cellulose nanomaterials from lignocellulosic biomass is still the most challenge. Because of the strong accretion of lignin, hemicelluloses, and other resources in plant cell wall, the biomass pretreatment is an important procedure for eradicating all non-cellulosic components. Nevertheless, such a pretreatment all the time includes complex steps, spent a lengthy time, and chomps toxic chemicals and produces wastewater. Furthermore, the universal techniques for the cellulose nanomaterials preparation from lignocellulosic biomass contain limitations such as, the high amount of acid waste water creation for the acid hydrolysis, extraordinary amount of energy consumption for mechanical process, and lengthy reaction time for enzymatic hydrolysis.

The enthusiasm on cellulose nanomaterials reports includes the expansion of innovative preparation techniques with a superficial stage and fewer or without wastewater generation. In the intervening time, the belongings and products of the resulted cellulose nanomaterials must cross over the conventional techniques. This innovative preparation technique is known as ball milling and a fascinating and imperative method for effective preparation of cellulose nanomaterialsfrom lignocellulosic biomass. No matter how the preparation of cellulose nanomaterials with the assist of ball milling has just started since early of 2010s, it must appeal to more consideration in the forthcoming research. In this context, it is important for both the preparation of cellulose nanomaterials directly from biomass and have valuable information for the mechano-chemical preparation of cellulose nanomaterials by ball milling.

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Lignocellulosic biomass, cellulose, nanocellulose, preparation, application.

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