ECOFRIENDLY STRATEGIES FOR THE PRODUCTION OF NANOCELLULOSE FROM AGRO-INDUSTRIAL WASTES

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ABSTRACT: The high exploitation of non-renewable resources has served as a motivation for an intensive research and development of new types of bio-based and degradable feedstocks derived from natural sources. Lignocellulosic biomass is rich in biopolymers, and can be obtained from several sources, among which are the residues from agricultural and industrial lignocellulosic crops. The cellulose extracted from the biomass can be fragmented giving rise to a nano-bio-based material - nanocellulose (NC). In recent years, studies on nanocellulose resulted in a wide range of applications. This work focuses on the recent developments about the valorization of lignocellulosic biomass obtained from different lignocellulosic agro-industrial crops, as a source of NC. Aspects discussed are (i) structure of lignocellulosic biomass and their influence on the nanocellulose properties (ii) more sustainablel biomass pre-treatments and nanocellulose extraction procedures, (iii) latest technological applications. A survey of the current knowledge is made in order to identify future opportunities of nanocellulose in the framework of a resource efficient bioeconomy.

Keywords: lignocellulosic sources, agroindustrial residues, pretreatment, nanocellulose, biobased products

1 INTRODUCTION

The continuous emissions of CO_2 into the atmosphere continues to be a reality that makes our society face day after day a deterioration of the ecosystem manifested by global warming. Inconsistent and uncontrolled consumption of non-renewable resources from the earliest years of industrialization has made the theme of environmental sustainability fundamental to be debated by the world's top governments [1]. In order to provide a better world for future generations, it´s extremely important to implement measures that mitigate the excessive use of non-degradable waste that causes a landfill overload and consequently pollution of the seas and oceans [2].

Giving a second life to agro-industrial waste could help to achieve the sustainable objectives proposed for the next years. Biomass wastes include wastes from agronomic crops (straw, bark, leaves, bagasse), energy crops, forestry crops (hardwood and softwood), or even food garbage and other residues from afro-food-industries that may contain high lignocellulosic content [3]. The lignocellulosic biomass wastes are a poorly utilized bio-resource. It is being used as feedstock for biofuels, biomaterials and chemicals, but the excessive amount produced per year (around 1.3×10^{10} metric ton) allows that new alternatives of value-added products could be exploited [4] [5] [6].

By entering in a new industrial age, the exploration of the world seen from a nanometric perspective is essential to unleash a technological revolution in interdisciplinary fields ranging from medicine, engineering, or even food and wellness. The study of new nanomaterials is very important not only because they have a much smaller dimension than usual but also because they have different physical, chemical or biological properties from the bulk material [3]. The development of nanotechnology in the area of biomass valorization has brought a new concept known as nanocellulose, giving rise to scientific and industrial interest. The interest on nanocellulose is mainly linked to the mechanical and barrier properties, to the high specific surface area, high crystallinity, biodegradability, renewability, and very low toxicity. Combining these characteristics with the low cost of production due to the high availability of biomass ven rise to interest on this material to be explored in a large number of applications [4] [7].

2 OBTAINING CELLULOSE FROM BIOMASS

Before reaching the nanocellulose, it is essential to study and understand the fundaments behind the structure of lignocellulosic fibers. The lignocellulosic biomass has a very complex architecture consisting of three primary structural units which are cellulose, hemicellulose, and lignin and also contains minor quantities of extractives like ash, pectin or waxes [3].

Cellulose presence in the fiber is typically between 35-50 wt% being not only the major single element of lignocellulose as the most significant, abundant and renewable biopolymer prevailing on nature. It´s defined for being a polydisperse linear homopolymer with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to many thousands of $\beta(1\rightarrow4)$ linked D-glucose units, including free hydroxyl groups (-OH) at the C-2, C-3, and C-6 atoms [8]. The cellulose chains are linked by Van der Waals and hydrogen bonds and are bundle into microfibrils, and these microfibrils are in turn bound to each other by hemicellulose and lignin. Crystalline packing emerges due to the lateral stabilization provided by the hydrogen bonds turning the cellulose molecules into a long-assembled bundle of aggregated and order domains. These order domains are linked by other disordered domains called amorphous [9], [10]. The second most plentiful polysaccharide represented in the plant cell walls is hemicellulose with an expected amount of 25-45 wt%. It's a heterogeneous and highly branched short chain polymer made up of five- and six-carbon molecules like pentoses (e.g. xylose), hexoses (e.g. glucose, galactose), and organic acids. Hemicellulose makes its point of contact with cellulose fibrils through hydrogen bonds and Van der Waal's interactions. Moreover, it also connects with lignin. These linkages between the three elements are related to the strength of the plant cell wall structure. Lignin, an aromatic, insoluble in water polymer, that contains in its structure three phenylpropane units (p-coumaryl, coniferyl and sinapyl alcohol), represents about 15–35 wt% of lignocellulosic biomass. Lignin has the binder function in the plant cell walls, holding between and around cellulose and hemicellulose. With this role, lignin confers higher mechanical properties, resistant to decay, and water impermeability [8].

Lignocellulose biomass has a complex matrix of different bonded constituents in which is very hard to overcome the resistance to deconstruction that plant cells offer. This difficulty to separate the highly crystalline cellulose from the lignin-carbohydrate complex is called recalcitrance. Besides the fact that higher amounts of lignin and hemicellulose make harder to trace a direct road to get cellulose, this difficulty is also connected with other biomass aspects like crystallinity, the polymerization degree, the accessibility to enzymatic degradation [3] [11].

In order to beat recalcitrance, it's necessary to apply a pre-treatment to biomass making cellulose accessible. Pre-treatments can be classified as chemical, physical, physicochemical, and biological, whereby each one has its own advantages and disadvantages [12]. Traditional chemical pre-treatments as acid or alkali-catalyzed are classified as the most efficient ways to treat biomass in terms of operation conditions facilities and economic expenses, but the coproduction of toxic by-products nurtures environmental concerns. Physical pre-treatments are known for having great results by increasing the accessibility, but when it is planned a scale-up to industry, the use of heavy machinery will consume a lot of energy which will allocate more costs to the process. Biological pre-treatments offers certain advantages since they are carried out under mild conditions, with low energy demand and without the release of toxic compounds, but these are still costly and time consuming [3] [13]. Thus, the efficiency and the suitability of the pre-treatment should be considered based on energy and time consumption, cost for chemicals and/or enzymes, initial capital for setting up the plant, the inhibitors released after the pre-treatment process, the waste generated from the pre-treatment process, the environmental impact, and the yield of cellulose isolated from the other compounds [11], [13]. Following the idea of sustainable pre-treatments, we will explore three different hypotheses that could be a better solution to be introduced in nanocellulose production protocols, replacing the traditional ones.

Ionic Liquids (ILs) are liquids formed only of ions, with an organic asymmetric cation and an organic or inorganic counterpart anion. Ionic Liquids are in the liquid state at temperatures under 100ºC [14]. Some ILs can be potential solvents for hardly soluble materials which cannot be dissolved by polar molecular solvents, such the dissolution of cellulose [15]. ILs are not only advantages but also have some adversities associated like the high cost and system complexity [16] [17]. Several types of IL'shave been tested over time and some provide an excellent cellulose dissolution capacity, such as a) BMIMCl - 1-butyl-3-methylimidazolium chloride; EMIMOAc - 1-ethyl-3-methylimidazolium acetate [18].

Steam explosion is a hydrothermal pre-treatment that take place in shorts periods of time in which biomass suffers an explosive physical break of the lignocellulosic complex increasing the accessibility to cellulose [19]. Normally, the materials are treated at 160-260 ºC with a steam pressure in the range 1-3.5 MPa, and at a time no longer than few minutes [12]. When compared with other traditional physical treatments, steam explosion demands less 70% energy consumption [12] [19].

Biological pre-treatment primarily uses bacteria and other microbes to decompose the lignocellulosic structure by hydrolases and other enzymes that depolymerize lignin [20]. Different bacteria and fungi species are being tested but the most frequently used are the white-, brown, and soft rot fungi, being the white-rot fungi the most promising [21]. Advantages of this approach lie on the milder conditions and on the low energy consumption needed [22]. In the future, with new technological and scientifically developments in the genetic engineering it's possible that bacteria and fungi could play a more relevant role as pre-treatment.

3 NANOCELLULOSE FROM CELLULOSE

Nanocellulose (NC) demonstrated more beneficial properties, such as better morphology, high specific surface area, or surface chemical reactivity, than bulk cellulose and microcrystalline cellulose (MCC), due to the nanosize [3]. To obtain nanocellulose from cellulose is a two-step process: pre-treatment application to deconstruct the lignocellulose complex and increase the cellulose accessibility and, in the second step, the cellulose is converted into nanocellulosic materials, cellulose nanocrystals/nanowhiskers (CNC/CNW) or cellulose nanofibers (CNF) [3].

The most common method to produce nanocrystalline cellulose is via acid hydrolysis, which digests the amorphous parts of cellulose, releasing a high crystalline rod or needle-shaped CNC [12], with variable dimensions (3-20 nm, wide, 50-500 nm, length). But, more eco-friendly methods should be developed in order to overcome the economic and environmental constraints of this process [3], [23].

Cellulose nanofibers (CNF) are composed of crystallized and amorphous regions, so this kind of nanocellulose is more long and flexible than CNC, presenting 5-100 nm, width and 500-2000 nm, length. Due to the higher length, CNF take advantage over CNC in applications like composite reinforcement [24], [25]. CNFs are obtained through mechanical processes, such as ball-milling or high-intensity ultra-sonication [3]. The high amount of energy needed for the process constitute the main constraint to the use of CNF by the industry [12]. The employment of certain pre-treatments, e.g. 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation, before the fibrillation may overcome this constraint [25].

4 NANOCELLULOSE APPLICATIONS

Polymer bionanocomposites are a new class of materials with broad applications for consumer, in industrial and medical fields and are defined as blends of a certain polymer (or biopolymer) reinforced with reduced quantities of nanofillers [26]. Nanocellulose as a biobased nanofiller can be applied easily to biocomposites due to its properties, including the low public health risks [27].

Food bionanocomposites packaging is one of the possible applications once the use of nanocellulose as reinforcement reduces the constraints associated with bioplastics (e.g. reduced mechanical strength) [3].

The characteristics of nanocellulose allow it to be considered as a material of excellence, paving the way for new discoveries in the area of biomedicine. The biocompatibility demonstrated by nanocellulose is a necessary requirement in biomaterials because it is necessary to ensure that an external material can be implanted in the body and coexist in harmony with the surrounding tissues. Properties such as hydrophilicity and polarity may limit the applicability of nanocellulose in this field, but thanks to the possibility of its surface being modified allows adaptation to different applications [7]. In addition to biocompatibility, another interesting property for this type of application is the low or even nonexistent toxicity of the nanocellulose. Many applications have been studied and highlighted such as drug delivery systems, tissue engineering materials, and other nanocellulose-based biomaterials [28].

Regarding electronic materials, nanocellulose has been exploited mainly as a substrate, also called nanopaper, thanks to its thermal stability and flexibility, transparency and biodegradability, thus demonstrating its potential to replace glass and plastic. As it is also a future low-cost material, when it is optimized, it will be possible to lower the production costs of transistors and thus open up a whole new world of cheap, flexible and disposable microelectronics [29]. At the technological research level, nanocellulose has been exploited also as energy storage devices, or sportswear or military equipment [29], [30].

5 CONCLUSIONS

The invention of new environmental and alternative friendly products to traditional fossil-based materials is a relevant issue. Mixing the characteristics of cellulose with nano properties results in a material with promising applications- This is mainly due to the CNC and CNF mechanical properties, its biocompatibility, and its biodegradability. Nowadays, the products from nanocellulose are limited by the low availability and high operation cost, yet, there is a growing interest in innovative solutions that may fit the requests of large-scale productive units. So, the quest for new pre-treatments that produces less hazardous and toxic waste at low cost for the nanocellulose production should be one of the main objectives of the future research in this area.

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8 ORGANISATIONS

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