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Industrial and crop wastes: A new source for nanocellulose biorefinery

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ABSTRACT

In recent years the nanocellulose has become an important topic for several research fields due to its renewability, availability, biocompatibility and different awesome properties. As occurs with first and second generation bioethanol, the investigation on nanocellulose is gradually going towards the indirect use of lignocellulosic biomass, i.e. the exploitation of different cellulosic residues and wastes produced from agricultural and industrial activities because of the wide availability and renewable character of these feedstocks. In the present review, an exhaustive bibliographic study was performed to prove the increasing interest on these new cellulose sources. Furthermore, and according to existing literature about nanocellulose obtaining, the new properties and possibilities that this new feedstock offers were discussed, and the advantages due to the use of this kind of raw materials were presented. Finally, overlooking the valorization of existing agricultural activities and industrial processes, a scheme of the proper use of these agricultural and industrial wastes as a future nanocellulose supply chain was proposed.

1. The nanocellulose: what, how and why?

1.1. The cellulose and its nanostructures

Cellulose is the most abundant polysaccharide on earth with approximately 10^9 tons produced annually by (Urruzola et al., 2014). It is a highly ordered polymer of cellobiose (D-glucopyranosyl-β-1,4-D-glucopyranose) chains aggregated by numerous strong intermolecular hydrogen bonds between hydroxyl groups of adjacent macromolecules, forming cellulose microfibrils. Cellulosic materials present crystalline domains (Fig. 1) separated by less ordered ones called amorphous regions that are potential points for chemical and biochemical attacks. Crystalline and amorphous domains are found in native cellulose fibers in variable ratios, as a function of the plant species, with the growing conditions or the part of the plant. For these reasons, the properties of cellulosic nanocrystals depend largely on the cellulose source (Bras et al., 2011).

Even though all cellulose nanostructures are made of the same biopolymer, the use of different raw materials and different extraction methods determine its properties and applications. Therefore, this renewable raw material can be used to obtain nanocellulose tailored to specific needs. Basically, there are two main families of nanosized cellulosic materials, namely: (i) cellulose nanocrystals (CNC) and (ii) cellulose nanofibers (CNF), respectively obtained by acid hydrolysis and mechanical disintegration. CNFs are in spaghetti-like highly entangled networks of nanofibers, whereas CNC are highly stiff rods. Both bear numerous hydroxyl groups at their surfaces.

Other family of cellulose nanoparticles that could be considered is the bacterial cellulose (BC). This type of nanocellulose is produced by *Gluconacetobacter xylinus* bacteria and its morphology can be engineered over length scales ranging from nano to macro by controlling the biosynthesis pathway (Gatenholm and Klemm, 2010; Klemm et al., 2009). This collagen-like emerging innovative material possesses very good mechanical properties, even if it contains up to 99% water. This new nanocellulose is considered as biomaterial with great potential for biological implants and for cell immobilization/support for tissue regeneration. However, specific bacteria and nutritional media are necessary and so their obtaining from industrial and crop waste is not possible. That is why this kind of nanocellulose will not be considered in this review.

1.2. The importance of the nanocellulose technology: a literature overview

In recent years, the increasing number of publications and patents (Charreau et al., 2013) focused on cellulosic nanoparticles clearly evidences the great importance of this topic in the emerging

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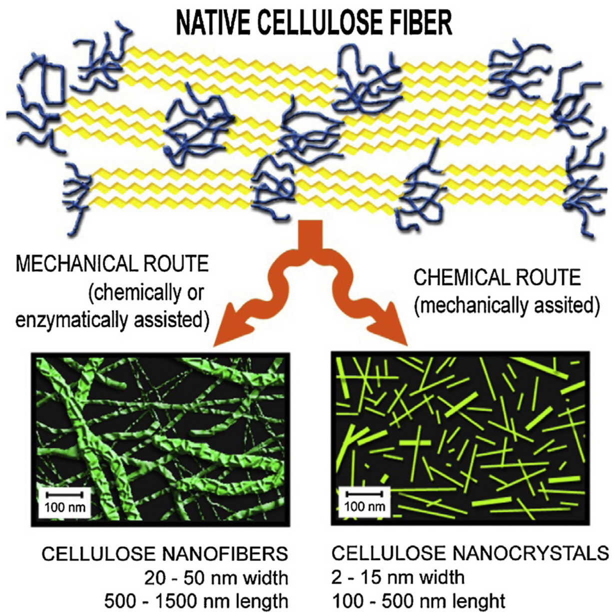

Fig. 1. The main nanocellulose families.

bio-based economy. An exhaustive and accurate overview of cellulose nanostructures concerning literature became complex and arduous due to the use of a wide and non-standardized terminology (Abdul Khalil et al., 2014; Charreau et al., 2013; Faruk et al., 2012; Keijsers et al., 2013; Lavoine et al., 2012). According to the SciFinder® literature research tool, scientific papers on the topic of nanocellulose rise considerably in the last four years. As presented in Fig. 2, which shows that the annual average of publications on this topic since 2010 is about 2500 documents per year, around 1000–1500 documents/year between 2005 and 2010, and less than 500 documents/year up to 2000.

While the majority of the pioneering works published in this area dealt with nanocellulose preparation and characterization (crystallinity, degree of polymerization, morphology...), today the major part of the published documents are related to the application of these nanostructures in nanocomposites (morphology, mechanical/thermal behavior), papers (coating, bulk addition), in various aqueous-based formulations (rheology modifier, food, cosmetics) or even in medical applications (scaffold, drug release). This difference shows a drastic change in the nanocellulose research field, and indicates a clear shift towards the industrialization and the development of new cellulose bio-based products. This fact is also evidenced by the increase of the ratio between patents and regular articles, as shown in Fig. 2.

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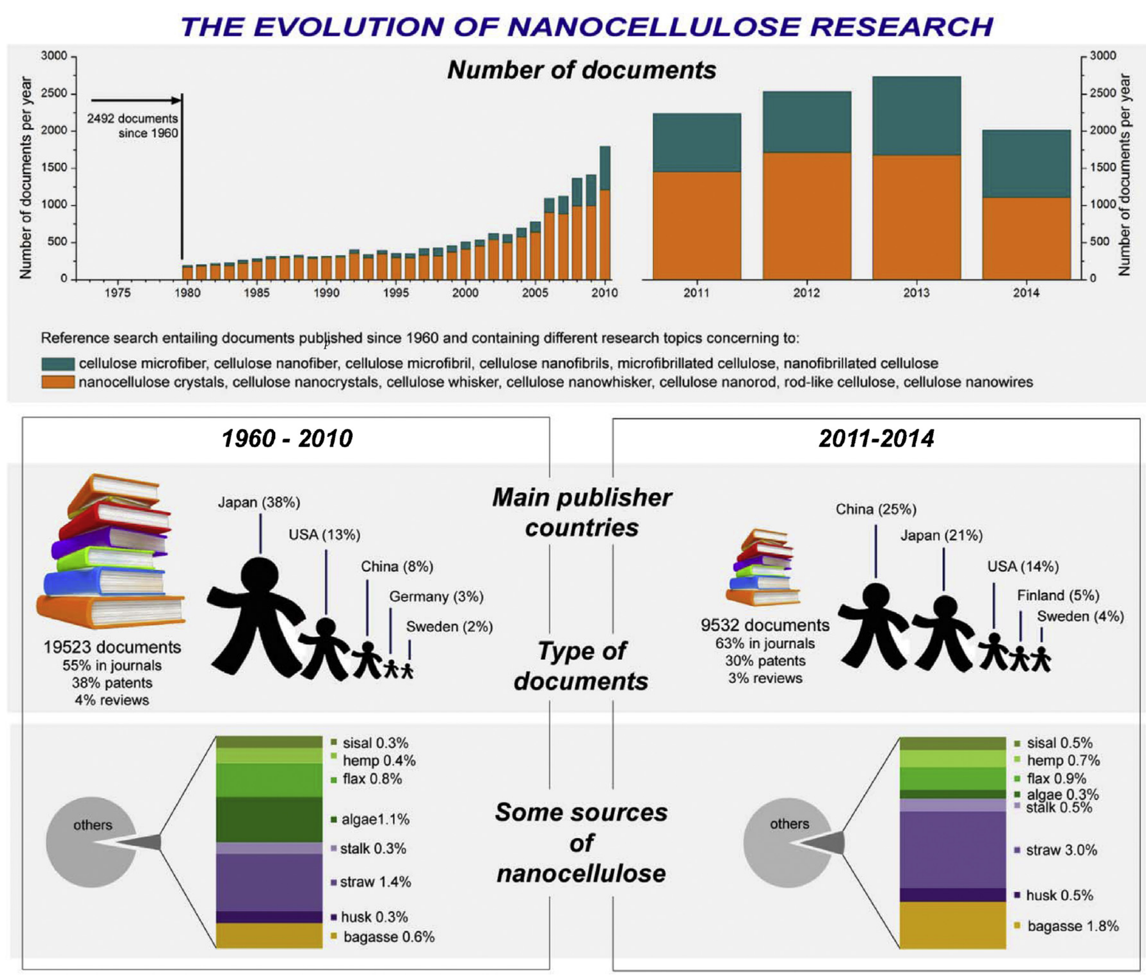

Fig. 2. The chronological analysis of nanocellulose research (source: SciFinder®, September 2014). Results were analyzed according to year of publication, document type and author company-organization, and refined by research topic for the studied cellulose source determination.