**REVIEW**

Plant and Bacterial Cellulose: Production, Chemical Structure, Derivatives and Applications

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**Abstract:**

Cellulose is one of the most abundant biopolymers in nature. It is used in the industry in various ways, in both its original and modified forms and the latter are called cellulose derivatives. These derivatives are used in several industrial such as the pharmaceutical, food, cosmetics and can be used in solid or semi-solid form. An important application that has been currently clarified is the use of some types of cellulose derivatives as adsorbents for both metal ions and other molecules. An example is the decontamination of wastewater, as with the industrial development, some water sources are compromised and decontamination by conventional means is often not enough, hence the need for new techniques. The main advantage of using natural polymers is that they are biodegradable, because it is extremely important that a product disappear after fulfilling its purpose. An example of a natural polymer is cellulose synthesized by bacteria, also known as bacterial cellulose (BC). It has been the subject of several studies in the last decade, mainly due to the fact that it is a highly pure polymer, which makes their physical and chemical properties very different from those of plant cellulose, and also because it is easy to produce, with yields varying from one bacterium to another. The aim of this paper was to gather general information about the structures, production mode, synthesis and industrial applications of bacterial, vegetable and cellulose derivatives.

**Keywords:** bacterial cellulose; biopolymer; cellulose; cellulose derivatives

**1. Introduction**

Cellulose was discovered in 1838 by Anselme Paven and materials arising from the chemical modification of this polymer emerged approximately 150 years ago, when in 1870 Hyatt Brothers patented a product synthesized. The product synthesized it occurred through of the reaction of cellulose with nitric acid, producing cellulose nitrate, a thermoplastic called celluloid that opened doors for the production of new cellulose-based materials, adding value to the textile, construction, ceramics, paints, cosmetics and/or food industries [1-2].

Studies show that cellulose is the most common biopolymer, representing approximately $1.5 \times 10^{12}$ tons of the world production of biomass per year and is also considered an unlimited source when it comes to more environmentally friendly products [3]. In recent years, cellulose has gained ground in the scientific world regarding research on the treatment of waste, once it is a renewable and easily available resource [4]. According to Silva Filho et al. [5], the research fields of inorganic materials or biopolymers is increasing, however, cellulose has advantages, because it is a renewable, abundant, inexpensive, biodegradable resource and can be produced by microorganisms other than plants.

The large number of publications regarding the subject evidences the great scientific interest. When searching Science Direct [6] for studies on the topic with the keyword *Cellulose*, we found a large number of results, which correspond to...
searches not only in polymers, but also in many fields, as shown in Figure 1. These results showed the increase of citations per year and the great importance of cellulose for the field of study. Thus, the importance of the subject for science as a whole is undeniable.

Cellulose can be obtained from other organisms besides plants such as algae, fungi, and some types of bacteria. Each organism produces this biopolymer with specific supramolecular structures, which are frequently studied in researches focused on the structure, crystallinity and reactivity of the biomolecule, besides the possibility to develop new biomaterials [3-5].

Bacterial cellulose (BC), also known as cellobiose, is a group that has been widely studied [7]. This kind of cellulose is produced from several bacteria, and the most studied currently is Acetobacter xylinum, which is gram-negative, rod-shaped and has aerobic metabolism [8]. Its structure resembles plant cellulose; however, it has a high degree of purity and crystallinity, ranging from 60% to 90% [9]. What differs cellulose from common synthetic polymers is mainly its sensitivity to hydrolysis and oxidation of acetalts, besides having a robust chain and many distinct functionalities; such characteristics determine its chemistry and manipulation [3].

Several times, cellulose can be modified into structures known as cellulose derivatives. These modifications are made according to what is wanted as final product, this is, the objective is to give cellulose different characteristics or intensify some of its properties [10]. Modification to obtain cellulose derivatives occurs in hydroxyl groups (-OH) due to their high reactivity. In order to obtain certain products derived from cellulose, there is constant difficulty in controlling the reaction, because most of the time, substitution of all OH groups takes place, which is not always interesting for the objective of the study. Such selective substitution has been the subject of several studies [11]. Cellulose esters, for example, are used in various separation techniques in the field of food and beverages, pharmacy, in scientific research, wastewater treatment, among others. These compounds perform all types of filtration, such as ultrafiltration, filtration of particles, nanoparticles, microparticles and hyperfiltration [12].

In view of the importance of cellulose and its derivatives, this paper aims to present a review on this polymer as well as its main industrial applications, forms of production and chemical structure. The article was organized as follows: Section 2 brings the structure of cellulose and its derivatives as well as the characteristics of each. Section 3 is on bacterial cellulose and synthesis. Section 4 is about the applicability and commercialization of cellulose. Section 5 is on cellulose as an adsorbent agent. Finally, the conclusions are found in section 6.

2. Structure of Cellulose and its Derivatives

Cellulose is the most abundant polymer in nature and is the main component of vegetable fibers, providing rigidity for plants [13]. It is a linear polysaccharide of long chain joined by β-1,4 glycosidic bonds, Figure 2 [14-17].

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In a monomer of cellulose, the functional groups are hydroxyls and a methanol group. The structure of the polymer is ordered, because the absence of side chains or branches is noted. In this sense, cellulose is a semi-crystalline polymer with crystalline and amorphous phases [13].
Cellulose is a polymer that, despite having a methanol group (-CH₂OH) at carbon 6 and hydroxyl groups (-OH) at carbons 2 and 3, both hydrophilic, does not dissolve when immersed in common solvents, because its side groups have strong hydrogen bonds with each other. The result of these interactions between units of glucose induces the formation of crystalline regions [17].

2.1 Cellulose derivatives

These compounds have been extensively studied and used in various sectors of industry, such as wastewater treatment, papermaking, food additives, pharmaceutical and textile applications [18]. There are several types of cellulose derivatives and the functions depend on the substituent group. Below are some cellulose derivatives.

2.1.1 Hydroxypropyl methylcellulose:

Hydroxypropyl methylcellulose (HPMC), Figure 3, is one of the most used hydrophilic biodegradable polymers, once it works as a gelling agent at any pH range. The HPMC has thickening and dilation properties being able to be used for controlled release of drugs [19].

![Figure 3. Hydroxypropyl methylcellulose with degree of polymerization n.](image)

A reaction between methyl chloride, sodium chloroacetate and cellulose must occur in alkaline medium to produce HPMC. The degree of substitution (DS) will interfere, directly, in its physical-chemical properties. Figure 3 shows a structure of HPMC with high degree of substitution and the hydroxypropyl radical ensures affinity with water through hydrogen bonding.

2.1.2 Carboxymethyl cellulose

Carboxymethyl cellulose (CMC), Figure 4, has applications in medicine, dyes, detergents and food. It has useful characteristics such as high viscosity at low concentrations and can work as an anti-foaming surfactant agent.

![Figure 4. Carboxymethyl cellulose with degree of polymerization n.](image)

To produce this polymer, a reaction between sodium monochloroacetate (ClCH₂-COONa) and cellulose must occur in a medium containing sodium hydroxide (NaOH). This compound, as well as HPMC, has affinity with water due to the carboxymethyl groups [11].

2.1.3 Cellulose xanthate

Cellulose xanthate (CX), Figure 5, also known as Viscose, may be produced by the reaction of cellulose with carbon disulfide in caustic medium, and it is insoluble in water [20]. Xanthate is basic, therefore, when compared to pure cellulose, it has greater capacity of ion-exchange or adsorption, which indicates a possible application as an efficient adsorbent of heavy metals [21].

![Figure 5. Cellulose xanthate with degree of polymerization n.](image)

CX is insoluble in water, that is, it is hydrophobic. However, the high sulfur content in the molecule indicates that the structure can develop sulfide interactions. Figure 5 shows
xanthate with DS of 100%.

2.1.4 Cellulose nitrate

Cellulose nitrate (CN), Figure 6, has many applications, which explains why it is known for being versatile. The maximum level of nitrogen in the cellulose nitrate is 14.4%, which means the substitution of the three hydroxyls available in the pyranose rings per nitrate. In this case, the main application would be in explosive formulations. Studies show that CN is considerably sensitive to UV light and heat, being decomposed and losing its nitro groups in decomposing and degradation reactions [22].

![Figure 6. Cellulose nitrate with degree of polymerization n.](image)

The cellulose derivatives are a result of substitutions at hydroxyl groups of each glucose ring for other functional groups, then, these compounds become less crystallized [23]. The degree of substitution of the hydroxyls of cellulose is not uniform and its commercial function will depend on how the substitutions are distributed in the polymer.

3. Bacterial Cellulose

The most explored cellulose currently is the naturally obtained from wood; however, besides plants, several living beings also work as sources of cellulose, such as mosses, algae, sea animals and some bacteria. In the latter case, the best known is of the *Gluconacetobacter* genus [24]. Besides having molecular formula identical to that of plant cellulose, bacterial cellulose (BC) has very different physical and mechanical properties. The difference between the celluloses occurs because the nanofibrils of the BC are thinner with a width of approximately 1.5 nm, thus increasing the area/surface/volume ratio, improving their water retention capacity, elasticity, high strength and formability [24].

Bacterial cellulose forms long nanofibrils of approximately 1.5 nm in its initial chains. When compared to the fibrils of plant cellulose, BC nanofibrils have greater surface area. BC also has subfibrils which, later, are crystallized into microfibrils forming bundles of microtapes [13-15]. The bacterial cellulose has a smaller microtapes diameter, it is metabolically inert, in addition to not being toxic or allergic [25]. The width of such microtapes is of approximately 1 to 9 nm, and they stabilize through hydrogen bonds, forming a dense, cross-linked and stabilized structure [24].

When it comes do BC, *Gluconacetobacter xylinum* is the most studied bacterium, because it produces cellulose from a wide range of carbon sources [26]. Production of cellulose by *G. xylinum* happens in three different ways as observed in Figure 7: a) through the pentose phosphate pathway, b) Krebs cycle, c) or when glucose enters directly into the cytoplasm transported by the enzyme glucose permease and such process will depend on the physiological state of the cell associated with gluconeogenesis [24].

The synthesis process of BC requires an energy expenditure of about 10% of the ATP generated in the cellular metabolism. This implies that microorganisms that produce BC must have an aerobic metabolism because they generate a greater balance of energy in the form of ATP. The conversion of glucose to cellulose, when the former comes from the extracellular medium, is catalyzed by a group of four enzymes. First, Glucokinase promotes the phosphorylation of carbon 6 of glucose, converting it to glucose-6-phosphate. Second, Phosphoglucomutase catalyzes a reaction of positional isomerization of glucose-6-phosphate into glucose-1-phosphate. Third, UDPG-pyrophosphorylase synthesizes UDP-glucose (UDPG). Lastly, the Cellulose Synthase (CS), which synthesizes cellulose from UDPG [17].

Another very important compound is the cyclic diguanylate monophosphate (c-di-GMP), an allosteric regulator. This regulator is, actually, an activator of CS, because, in the absence of c-di-GMP, cellulose synthase is inactive or has low activity [24].
4. Cellulose Applicability and Trade

Approximately 2% of all cellulose produced is used for the synthesis of some types of esters and ethers, as well as the production of fibers and regenerated cellulose films. Thus the cellulose is mostly produced by plants, it is an abundant biopolymer in nature, and due to its properties, it has many functions in the textile, pharmaceutical, cosmetic, food and paper industries, among others [27, 28].

4.1 Paper and cellulose industry

The Brazilian paper market, in the period from 2004 to 2014, had an increase of approximately 3% per year, which, consequently, triggered an increase in cellulose consumption. Brazil stands out as the largest paper producer in South America, as a growth rate of 2% per year is estimated for the paper market in this region in the period from 2014 to 2030 [29].

In Brazil, the most common species planted for the paper industry is eucalyptus, because it is fast-growing, and is used to generate printer and sanitary paper, among others which have low tear resistance. In 2008, the main groups responsible for the production of paper were: Klabin, Suzano, Internacional Paper and Votorantim Cellulose and Paper. That year, 9.41 million tons of paper were produced in Brazil and these companies were responsible for 41.2% of the production of this total [30].

4.2 Application of cellulose in the textile industry

The diversity of fibers used by the textile industry is divided into two categories: natural fibers and chemical fibers. Within the concept of chemical fibers, there is the distinction between artificial and synthetic fibers. Natural fibers can be of animal origin, with emphasis on wool and silk, or of plant origin, especially cotton [31].

For the manufacturing of synthetic and artificial fibers, a number of chemicals are used. For the production of synthetic fibers, the raw materials used are chemicals from the petrochemical industry. As for the production of artificial fibers, the raw material used is of natural origin, generally obtained from the chemical modification of cellulose [32].

Natural and synthetic cellulose, cellulose acetate and cellulose xanthate, Figures 2, 8 and
5, respectively, are among the foremost fibers from cellulose that are used in the textile industry [33].

![Figure 8. Cellulose acetate with degree of polymerization n.](image)

4.3 Application of cellulose in the cosmetic and pharmaceutical industry

Natural cellulose and its derivatives are widely used in the pharmaceutical and cosmetic industries, and can be used from packaging to drug delivery systems [34].

Since 1930, the pharmaceutical industry has used cellulose as a disintegrating and diluting agent of tablets. An important modification in cellulose that triggered its use as an agent of direct compression of tablets was the isolation of the crystalline part. To perform the isolation, alpha-cellulose undergoes acid hydrolysis after mechanic treatment, which yields the microcrystalline cellulose (MCC) [35].

MCC is used in medications because it is non-toxic, inert, and offers tablet hardness, has favorable compressibility and easy disintegration [36]. Other cellulose derivatives that also stand out in the pharmaceutical and cosmetic industry are methylcellulose (MC), Figure 9 and carboxymethyl cellulose (CMC), Figure 4 [37].

The biopolymers are also used in order to produce hydrophilic gels because they are not greasy and have better dispersion and low toxicity and low cost [34].

![Figure 9. Methylcellulose with degree of polymerization n.](image)

4.4 General applications of cellulose

By searching the Science Direct [6] website for the main applications of cellulose, we observed that most of the research on cellulose is related to protein, enzymes and amino acids, representing 29% of the research. Another important point observed is the beginning of studies focused on the health area with approximately 5% of research on the treatment of diseases [36-37]. For example, the treatment of breast cancer using oxidized regenerated cellulose to remodel and fill the lack of volume in breast-conserving surgery [37].

5. Cellulosic Materials as Adsorbent Agents

As a result of increased technology and life expectancy of the population, great development of the industrial and agricultural sectors has occurred in the last years, which led to the introduction of several types of pollutants into the environment, mainly soils and the aquatic environment. Among these pollutants are organic substances, inorganic anions, heavy metals and micropollutants. To remove this great amount of pollutants, due to their different structural matrices, several techniques are currently necessary [13]. In the last decade, several researchers have pointed to the adsorption technique as a great potential for pollutant removal, which indicates a large increase in research using pure cellulose or modified as adsorbent matrix. Table I shows research on which cellulose and its derivatives were applied to adsorption processes.

![Figure 10. Main applications of Cellulose.](image)
Table 1. Adsorption capacity of metals on several cellulose derivatives: (a) cellulose nanofibers incorporated with acrylic acid; (b) modified microfibrillated cellulose (MFC) and aminopropyltriethoxysilane (APS) in aqueous solution; (c) carboxymethyl cellulose fiber; (d) modified cellulose containing copper.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Ph</th>
<th>Adsorbate</th>
<th>Maximum adsorption capacity</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>PAA-cellulose&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>Cd(II)</td>
<td>162.5 (mg/g)</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu(II)</td>
<td>2.74 (mmol/g)</td>
<td></td>
</tr>
<tr>
<td>APS/MFC&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5</td>
<td>Cd(II)</td>
<td>3.45 (mmol/g)</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni(II)</td>
<td>2.63 (mmol/g)</td>
<td></td>
</tr>
<tr>
<td>ECMCF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6</td>
<td>Cd(II)</td>
<td>150.60 (mg/g)</td>
<td>[40]</td>
</tr>
<tr>
<td>Cell-N-Cu&lt;sup&gt;d&lt;/sup&gt;</td>
<td>8.4</td>
<td>As(V)</td>
<td>98.9 (mg/g)</td>
<td>[41]</td>
</tr>
</tbody>
</table>

The adsorption process consists of fixing a compound onto the surface of an adsorbent. These processes are classified according to the phases that constitute the system, which can be liquid/gas, solid/gas, solid/liquid and liquid/liquid. The adsorption can also be classified according to the type of adsorption, being of three kinds, physics (physisorption), chemical (chemisorption) or ion exchange.

Adsorbents obtained from the chemical modification of cellulose such as carbon, hydroxyls, ethers, esters and nitrates are mostly responsible for the strength of intermolecular interactions, that is, the adsorbent groups [38-41].

Chemisorption refer to chemical bond, which can be of metallic, ionic or covalent type. In physisorption, the adsorbates (pollutants) accumulate on the surface of the adsorbent by intermolecular forces. In this case, the main forces that control adsorption are van der Waals forces and hydrogen bonds. [13].

Cellulose-based products are used in a variety of separation techniques in the pharmaceutical and food and beverages fields, scientific research, wastewater treatment, among others. Cellulose ethers and esters are the most widely used nowadays, because they are able to perform all sorts of filtering as ultrafiltration, filtration of particles, nano particles, particles, and hyperfiltration [12]. They display a good ability to adsorb heavy metals and other pollutants. Unmodified cellulose has an adsorption property; however, it is a fact that when chemically modified, it presents higher capacity to adsorb various pollutants [13].

The most classic example of cellulose-based adsorption used is the case of diethylaminoethyl cellulose (DEAE-C), Figure 11, used in the ion-exchange chromatography technique. This occurs because the amino group is positively charged and can bond to the negative groups. It is a column chromatography used to purify negatively charged proteins or nucleic acids. In this case, the adsorbent captures the adsorbate and they are released when the concentration of salt in the solvent is increased to balance the charges.

![Figure 11. Chemical structure of DEAE-C, diethylaminoethanol groups are protonated, showing affinity with negative ions.](image)

6. Conclusions

For decades, cellulose has been one of the most promising polymers in scientific innovation for the development of new products and solution of environmental problems, because it is a very abundant renewable polymer, and of easy chemical modification.

Cellulose can be obtained in different ways, being plant cellulose the most abundant and bacterial cellulose. In the case of BC, it is important to stress that the fermentation process required for its production depends on the microorganism used as already described in the literature. It is worth highlighting that these bacteria are aerobic and require a large expenditure of ATP, i.e., the carbon source...
chosen should be used in optimal dosages.

There are many derivatives of cellulose and among the most important are the cellulose esters, ethers and acetates, as well as cellulose xanthate and nitrate. Their applications will depend on the kind of substituent at the hydroxyls and on their degree of substitution of hydroxyl. All forms of cellulose including natural, synthetic and their derivatives have very diverse industrial applications, having roles in industries of paper, cosmetics, and in the pharmaceutical and food industry.

In addition to its countless applications, cellulose also reappears as an alternative to control pollutants through the adsorption technique, once the more the world develops the more pollutants are disposed in springs. Therefore, from what was shown in this review, cellulose significantly contributes to the development of the industry in several fields, thus, showing the importance of more studies that elucidate its structure and composition, whether it is of animal or plant origin.

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References and Notes

[7] Ummartayotin, S.; Manuspiya, H. Renewable Sustainable Energy Rev. 2015, 41, 402. [Crossref]
[10] Casaburi, A.; Rojo, U. M.; Cerrutti, P.; Vázquez, A.; Foresti, M. L. Food Hydrocolloids 2018, 75, 147. [Crossref]
[12] Hokkanen, S.; Bhatnagar, A. Water Res. 2016, 91, 156. [Crossref]
[19] Ghorpade, V. S.; Yadav, A. V.; Dias, R. J. Int. J. Biol. Macromol. 2016, 93, 75. [Crossref]
[25] Lee, K. Y.; Buldum, G.; Mantalaris, A.; Bismarck, A. Macromol Biosci. 2014, 14, 10. [Crossref]
[27] Shokri, J.; Adibkia, K. Application of Cellulose and Cellulose Derivatives in Pharmaceutical Industries. Licens InTech. 2013, 47 – 66, chapter 3. [Crossref]
[29] Montebello, A. E. S.; Bacha, C. J. C. Economic Studies 2013, 43, 109. [Crossref]
[32] Quim. Nova 2015, 38, 1140. [Crossref]


[37] Chitpong, N.; Husson, S. M. *J. Memb. Sci.* 2017, 523, 418. [Crossref]

[38] Hokkanen, S.; Repo, E.; Suopajarvi, T.; Liimatainen, H.; Niinimaa, J.; Sillanpaa, M. *Cellulose* 2014, 21, 1471. [Crossref]

[39] Wei, W.; Kim, S.; Song, M. H.; Bediako, J. K.; Yun, Y. S. *J. Taiwan Inst. Chem. Eng.* 2015, 57, 104. [Crossref]

[40] Yousif, A. M.; Zaid, O. F.; Ibrahim, I. A. *Arab. J. Chem.* 2016, 9, 607. [Crossref]