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Bacterial Cellulose: A Review on Applications of Nanomaterials in Adsorptive Processes of Contaminated Environments

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ABSTRACT

Bacterial cellulose, also understood as an alternative method of ion removal through adsorption, is the subject of study in this literature review. This was based on the assumption that scientists are looking for effective methods to promote the reduction of environmental pollution, especially concerning toxic metal ions, as they significantly impact the fauna and flora of both the marine environment and fresh water, that is, anthropogenic activity throws in nature inorganic contaminants that need to be properly used in order not to increase the levels of metal ions in water bodies. Thinking about how to understand an effective solution that generates biopolymer productivity, through a qualitative methodology develops a bibliographic review pointing to bacterial cellulose as an absorbent capable of effectively separating heavy metals due to its purity, elasticity, and biocompatibility. Thus, it was intended to contribute to the debate on the application of such type of cellulose in the removal of metal ions from contaminated environments by means of reagents and microbial nanocellulose to score adsorption as an effective alternative.

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INTRODUCTION

Environmental pollution caused by the contamination of potentially toxic metal ions present in rivers and lakes, which originated mainly from industrial effluents, is one of the world's problems to be solved. Some heavy metals are characterized, in certain concentrations, as natural constituents of the environment, thus, contaminations involving these metals alter the levels of usual (normal) concentrations directly and negatively impact the fauna and flora present in marine and freshwater environments.[1] These inorganic contaminants originate from anthropogenic activities (industrial, domestic, agricultural, medical, and technological applications) that inevitably increase the levels of various metal ions in water bodies.[2-3]

In recent years, there has been a great concern on the part of researchers, who are dedicated to the research of new materials capable of presenting themselves as viable technologies for the remediation of these contaminants. Thus, different methods of removal of metal ions from wastewater were also developed, including chemical precipitation, ion exchange, flocculation, membrane filtration, electrochemical treatment, adsorption, and others.[4-5] The use of heavy metal adsorbent materials is considered a promising and effective process since some renewable natural materials are used and prone to chemical modification for greater adsorption.[6] As an example, cellulose or cellulose-based materials are included, covering some agro-industrial waste, which has been applied for the removal of heavy metals.

Bacterial cellulose (BC) has the same chemical composition as vegetable cellulose (VB), that is, both are formed by glucose molecules joined by glycosidic bonds.[7] However, they differ in the size of the fibrils formed, the structure of BC that is devoid of lignin, hemicellulose, and pectin with high purity that has nanocrystalline domains when compared with plant cellulose.[8] In addition to these properties, it is worth highlighting the comparison of the productivity of BC and VB, an essential attribute to determine the advantage of producing cellulose from bacteria.

The first report on bacterial cellulose formation occurred in 1886 by researcher Adrian Brown who described the formation of a gelatinous film on the surface of an apathetic fermentation process.[9] The analysis of this material revealed that the cellulose formed was produced by *the bacterium Acetobacter xylinum*, in which its nomenclature was confirmed at the meeting of the ICSB judicial committee on March 29, 1973[9-10], currently reclassified as *Gluconacetobacter*

xylinus, based on the phylogeny of the 16S rRNA sequence and phenotypic, ecological and chemotaxonomic characteristics.[11] In 1931, Hibbert and Barsha analyzed the chemical composition and structural properties of BC and found that BC was identical to cellulose of plant origin in the molecular formula, although it had unique properties compared to plant cellulose.[12] Once its properties have been examined, it has gained increasing attention and has been widely explored in recent decades by the scientific community.[8]

In this analysis, researchers compared pulp production from 1 ha of eucalyptus with an average annual increment of $50m^3$, providing a basic density of $500kg.m^{-3}$, generating an average annual increment of 25 tons. of $cellulose ha^{-1}$ $year^{-1}$. After 7 (seven) years of this planting, 45% of cellulose content was produced, generating 80 tons. Ha-1cellulose. These authors found that the same product could be obtained by bacteria, with a hypothetical yield of 15 $g.L^{-1}$ in 50 h of cultivation (average of 0.3 $g.h^{-1}$) in a 500 m^3 bioreactor for approximately 22 days. With this, in addition to having a more efficient production, there is pure and ecologically sustainable bacterial cellulose as a product.[13]

Bacterin cellulose is a more abundant biopolymer consisting of monomeric units of β-D-glucopyranose called cellobiose, which is converted into polymeric cellulose, through the joining of glucose units by β(1→4) glycosidic bonds, generating non-branched linear chains, which are connected through van der Waals forces and hydrogen bonds.[14-16]BC has enormous potential to be used as a new adsorbent for effective separation of heavy metals due to its properties of high water retention capacity, fine fiber network, high resistance to mechanical traction, high purity, flexibility, elasticity, absence of toxicity and biocompatibility.[17] However, pure BC is not suitable for the adsorption of a huge variety of metal ions as a result of lower adsorption and selectivity capacity in some cases. Thus, the synthetic strategy of modification of cellulosic matrices, which allows the inclusion of new functional groups capable of improving adsorption activity, has become promising and is characterized as a widely studied line of research.[18]

Due to these peculiar properties, the most common applications of BC are biomedicine, the food industry, pharmacology, cosmetics, electronics, and textiles. According to Shi *et al.*[19], applications of new BC-based materials are sought for applications in nanotechnology, biotechnology, immobilization, adsorption, catalysis, and engineering, in which hydrogels,

membranes, composites, nanofibers, nanocrystals, and other various products or technologies involving BC are developed.

Thus, the purpose of this review article is to contribute to the discussion on bacterial cellulose and applications of modified bacterial cellulose (MBC) in absorbing processes for the removal of metal ions in contaminated environments focusing on articles published in journals in recent years, to synthesize knowledge on the subject.

MATERIALS AND METHODS

To develop a critical analysis of the use of modified bacterial cellulose in absorbing processes that promote the removal of metal ions in contaminated environments, a descriptive qualitative methodology was developed, using the literature review as the main methodological procedure. However, it should be understood that the literature review focused specifically on scientific articles that worked on the theme through two active methodologies to reagents and Microbial nanocellulose, described below:

Reagents

The strain used for bacterial cellulose membrane growth was *Gluconacetobacter xylinum* (ATCC 23769) supplied by the Biotechnology Laboratory of the Center for Strategic Technologies of the Northeast (Recife, Brazil). Yeast and peptone extract was purchased from HiMedia BioSciences Company (Mumbai, India). Anhydrous bibasic sodium phosphate (Na_2HPO_4) and succinic acid were acquired from The Modern Chemistry Industry and Commerce (São Paulo, Brazil), and glycerin was acquired from Labsynth (São Paulo, Brazil). All chemicals were analytical in grade and used without additional purification. Bi-distilled water (DDH_2O) was used in all experimental procedures.

Microbial nanocellulose

The production of the bacterial membrane is used by the bacterium *Gluconacetobacter xylinus* and as a carbon source glycerol. The culture medium was produced with 30 $g.L^{-1}$ of glycerol, 16 $g.L^{-1}$ of yeast extract, 5 $g.L^{-1}$ peptone, 4 $g.L^{-1}$ of Na_2HPO_4, and 3.5 $g.L^{-1}$ of succinic acid. The volume was distributed in previously autoclaved borosilicate glass bottles at 121°C for 15

minutes. For incubation, 5mL of *Gluconacetobacter xylinus* was pipetted for Hestrin and Schramm (HS) medium for 48h under static conditions at 30°C. After obtaining the membrane, purification was immersed in a NaOH solution (0.1 mol.L^{-1}), under heating at 80°C for 30 minutes. The process was repeated until the pH reached around 7.

RESULTS

Bacterial Cellulose Structure

Bacterin cellulose is characterized by presenting a structure in the form of a three-dimensional network, where the chains are grouped through connections of hydrogen bridges forming the microfibrils, which aggregate to form the cellulose fibrils and are then ordered to form the cell wall of the fiber.[20] The bonds involved in the composition of the cellulose structure are: intramolecular, which occur between the hydroxyl groups of the same chain conferring a rigidity of cellulose, and the intermolecular bonds that occur between adjacent hydroxyl chain groups, and are responsible for the formation of the supramolecular structure acquiring great tensile strength.[21]

The microfibrils, which make up the fibers, consist of two distinct regions. One of these regions is formed by highly ordered cellulose chains with a dimension ranging from 1-100nm, known as crystalline regions and the other region consists of disordered chains, known as amorphous regions.[22] According to Jesus Silva and D'almeida[22], the formation of crystalline regions is related to the polymerization and crystallization of cellulose commanded by enzymatic processes, but the emergence of amorphous regions is related to the malformation of crystalline structures, known as regions in which crystallization occurred with the defect.

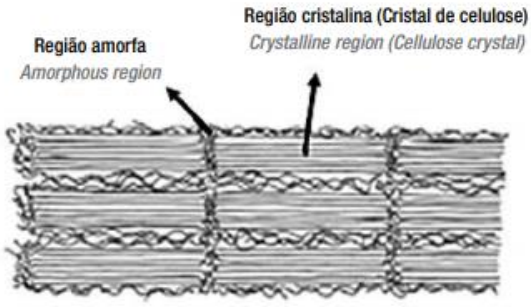

Figure 1. Cellulose morphology. Source: Jesus Silva and D'Almeida.[21]

The BC presents a degree of crystallinity between 60 and 90%, considered high, compared with that of plant cellulose which is 40% to 60%. The proportion between the crystalline and amorphous regions, which determines the degree of crystallinity and dimensional characteristics of the crystalline domains of BC varies according to their origin and pretreatment.[23]

Cellulose nanocrystals (CNCs) are crystalline domains of cellulosic fibers obtained through acid hydrolysis. The crystalline regions of the cellulose structure are insoluble under the conditions used because cellulose has a high molecular organization in its nanostructure.[22] On the other hand, the natural disorder of cellulose in the amorphic regions makes acid accessible and, therefore, breaks the cellulose chains, because in this region it presents less stereochemical impediment and lowers cohesive forces of hydrogen bonds and Van der Waals than in the crystalline regions.[21]

Acid hydrolysis begins with the protonation of glycoside oxygen (Figure 4.a), followed by the destruction of the C_1-O bond (Figure 4.b). The carcarbocátion generated in step b can be stabilized by the repositioning of the existing electron pair in the oxygen of the glycoside ring that is adjacent to carbon 1. The nucleophilic attack of water in C_1 (Figure 4.c) through acid regeneration (Figure 4.d and 4.e) terminates the depolymerization phase (if it occurs within the cellulose chain, new extremities are produced) or glucose production (when hydrolysis occurs directly at the extremities).[24] The result of this process is the obtaining of cellulose nanocrystals, where their sizes depend on hydrolysis conditions, such as concentration and type of acid, time, temperature, and cellulose source.[25]

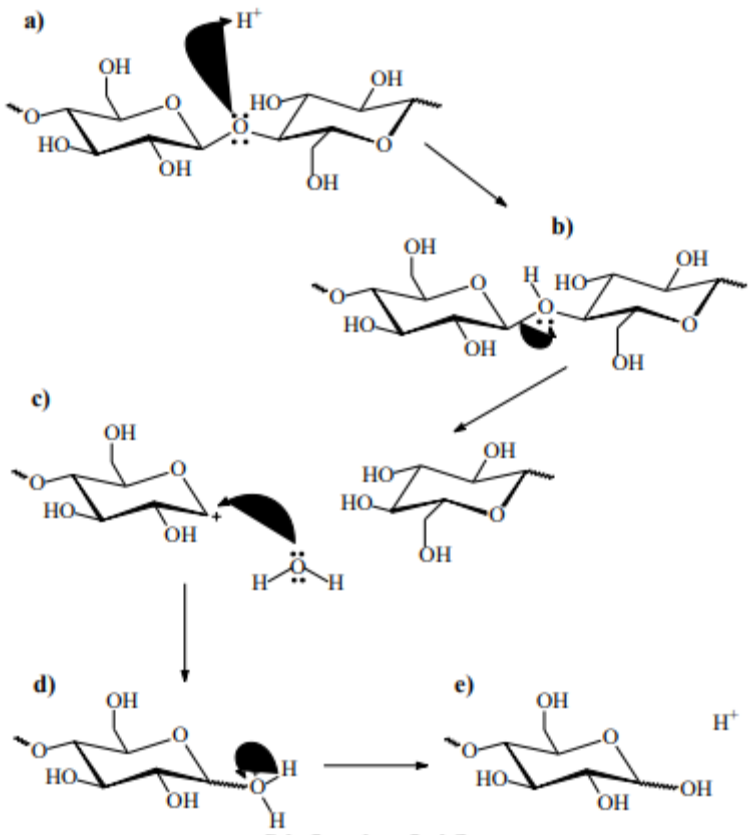

Figure 2. Mechanism of cellulose hydrolysis in the acid medium for CNCs formation. Source: Ogeda and Petri.[25]

Table 1 shows the length and width of cellulose nanocrystals from different cellulose sources and hydrolysis conditions. It can be observed that CNCs obtained from bacterial cellulose is generally larger in dimensions than those derived from lignocellulosic material. This is because bacterial cellulose is highly crystalline, so there is a small portion of amorphous regions, resulting in larger nanocrystals.[26]

Table 1. Dimensions of CNCs prepared from different sources.

Source	**Length (nm)**	**Diameter (nm)**	**Reference**
Bacterial Cellulose	200-1000	16-50	Vasconcelos *et al.*[27]
Cotton	100-150	5-10	Araki *et al.*[28]
Wheat straw	150-300	4-5	Dufresne *et al*[29]
Rice straw	117	8-14	Ping e hsieh[30]
Coconut fiber	172	8	Nascimento *et al*[31]
Wood	120-170	4,5-7,5	De Mesquita *et al.*[32]

The main acids used in the isolation of CNCs are sulfuric acid and hydrochloric acid. The isolation of cellulose crystals with sulfuric acid was first reported by Ranby in 1951, when highly stable colloidal suspensions were produced, as the sulphonation process produces a large number of negative charges on the surface of cellulose nanocrystals facilitating dispersion in water. On the other hand, a large number of sulfated groups on the cellulose surface catalyzes the decomposition reaction of nanocrystals, leading to a decrease in the temperature of thermal degradation. Despite the low load density and, therefore, suspension instability, hydrolysis with hydrochloric acid will still produce nanocrystals with greater thermal stability due to the absence of sulfated groups.[27]

However, other acids can also be used for the extraction of cellulose nanocrystals, arranged in Table 2 with their hydrolysis conditions.

Table 2. Research for the extraction of cellulose nanocrystals

Source	**Type of Acid**	**Hydrolysis conditions**	**Reference**
Bacterial Cellulose	H2SO4 50%, 60% e 65% (m/m)	60 minutes, 45°C	Vasconcelos *et al.*[27]
Cotton	HBr 2,5 M	180 minutes, 100°C	Sadeghifar *et al.*[33]
Cotton	H3PO4 85% (V/O)	90 minutes, 100°C	Espinosa *et al.*[34]
Bamboo	HNO3 30%+ KClO4 10% (m/m)	24 hours, 50°C	Liu *et al.*[35]

Acid hydrolysis using hydrochloric acid is less common to hydrolysis with sulfuric acid. However, studies have been developed in obtaining nanocrystals through combined acids (sulfuric and hydrochloric), producing more NCC with more stable suspensions and with more thermal resistance.[31,32,36]

Studies conducted by Teixeira *et al.*[37] applied the process of hydrolysis of combined acids (1:1; sulfuric acid: hydrochloric acid) in nanofibers of commercial cotton. The results showed that the morphology and crystallinity of the nanofibers are similar, regardless of the acid used in hydrolysis. On the other hand, the main difference found was that the incorporation of HCl into H_2SO_4proved to be effective in increasing the thermal stability of cellulose nanofibers compared to those applied only with H_2SO_4.[35]

Bacterial Cellulose Biosynthesis

The structural properties of BC are influenced by the nanostructure of the material, a property directly related to the type of bacteria used in fermentation. Among all the microorganisms found in the literature capable of synthesizing BC, the most used *is Gluconacetobacter* xylinus, which has been considered a model microorganism for biosynthesis studies, due to its ability to produce cellulose in the presence of different sources of carbon and nitrogen.[33-38]

The synthesis of CB from *Gluconacetobacter* xylinus consists of a process that involves three main steps. The first step concerns the polymerization of glucose residues in a 1→4β glycan

chain, followed by the step that corresponds to the extracellular secretion of linear chains, and finally refers to the crystallization of glucan chains using hydrogen bonds and Van der Walls forces.[34, 39, 40]

The biosynthesis process of BC involves several biochemical reactions, when glucose is used as a carbon source, the formation of cellulose chains occurs between the outer membranes and cytoplasmic membranes of the cell by the biocatalytic action of enzymatic complexes of cellulose synthesis from phosphoglucose uridine (UDPGlc).[41] The best known biochemical pathway is the polymerization of glucose in cellulose, plus other substrates can also produce bacterial cellulose, as shown in Figure 3. In this way, some specific enzymes are necessary to first convert glucose into ATP-dependent glucose-6-phosphate by the action of the enzyme glucokinase. In the second step, the enzyme phosphoglucomutase converts glucose-6-phosphate into glucose-1-phosphate through an isomerization reaction. After the conversion reaction, glucose-1-phosphate undergoes a reaction by enzyme-glucose pyrophosphorylase, responsible for the synthesis of uridine diphosphoglucose (UDPGlc). By using uridine triphosphate molecules, and releasing pyrophosphate molecules, UDP-glucose will be used as a substrate by the cellulose synthase enzyme to initiate the glucose polymerization reaction for bacterial cellulose production.[42] Lee *et al.*[38] explain that this polymerization reaction process is not yet fully understood by researchers, being a possible hypothesis.

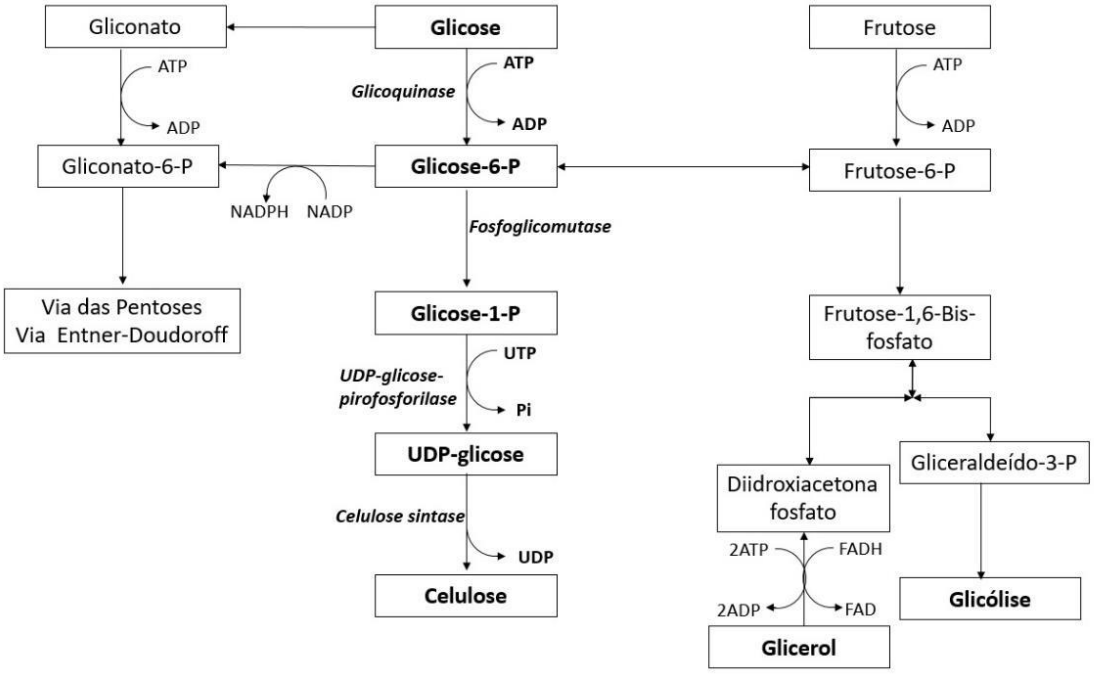

Figure 3. Biochemical pathways for the production of bacterial cellulose. Source: Adapted from Recrovreux.[42]

BC is regulated by the cellulose synthase enzyme, which is responsible for catalyzing the polymerization reaction of glucose molecules, which is activated by the cyclic adenosine molecule monophosphate (c-di-GMP), the c-di-GMP molecule is synthesized by the enzyme diguanylate cyclase from two molecules of guanosine triphosphate (GTP), c-di-GMP concentration is controlled by the phosphodiesterase enzyme that degrades the c-di-GMP molecule producing bacterial cellulose.[43]

BC begins to be formed when the bacterium originates chains that aggregate generating subfibrils with widths of approximately 1.5 nm, which are grouped with others forming an elemental fibrilla with a diameter of approximately 3-3.5nm. The fibrils join through hydrogen bridges *forming a ribbon*, ultra-thin structure reaching lengths between 1 and 9 μm, the name given to CB fibrils.[23]

DISCUSSION

In the production of BC, the most used culture medium is that described by Hestrin and Schramm[44], which is a synthetic medium that uses glucose as a carbon source, and as a source of peptone nitrogen and yeast stratum. The fermentative medium for BC production is usually composed of 2% m/v of glucose, 0.5% peptone, 0.5% m/v of yeast extract, 0.27% m/v of disodium phosphate (Na_2HPO_4) and 0.115% m/v of citric acid, with pH of approximately 6 (six).[45] However, other alternative sources have been studied and evaluated in an attempt to obtain better yields.

Bacterial cellulose can be synthesized by static and agitated conditions.[17] The choice of cultivation condition will depend on the applicability of the formed product, since some properties of BC may differ. In general, they are usually grown statically, using aerobic fermentation, produced at the air-liquid interface, which is incubated for several days until a membrane is formed on the surface, which increases in thickness with increasing cultivation time. Traditionally the crop is grown in shallow jars for a period of 5 to 20 days until the appearance of a film on the surface of the bottle. The film is then removed, and washed, usually with sodium hydroxide (NaOH) in a water bath at 80°C for the removal of bacteria, known as the purification process of BC.[42] Borzani and Souza[46] in their studies contacted a thin layer of cellulose that formed parallel to the surface of the culture medium, which confirmed what Fontana[47] described, because for this a new layer always appeared at the liquid-air interface and that nutrients diffuse through the innermost BC layer to the most active bacterial cells in synthesis.

The advantages of production in static cultivation are the low cost and because it is a simple method although it presents some disadvantages that do not lead to the process, such as control and standardization of the inoculum, monitoring the temperature and pH, and determination of the amount of oxygen dissolved in the medium.[47,44,48]

The BC produced under agitated conditions, with bioreactors or bottles with agitation, is presented in the form of small granules instead of film, which directly influences the yield of BC production, by the fact of providing greater aeration.[13] There are reports in the literature that, in agitated crops, there are formations of spontaneous mutations, where cellulose-producing strains

are transferred to spontaneously agitated cultures, they become non-producing bacteria, resulting in the reduction of the degree of polymerization and the degree of crystalline and mechanical resistance compared with BC produced under static conditions.[44,49,50]

Several factors influence the production and properties of BC from the choice of microorganism used to the temperature, pH, dissolved oxygen in the medium, and composition of the medium because they cause microorganisms to respond quickly to induction or inhibition of protein activity and changes in cell morphology. According to Ruka *et al*.[51], determining the ideal environment and growth conditions to enable high levels of pulp production will add the characteristics needed to extend the technology to industrial environments.

Temperature is an important parameter for conducting the BC production process. Son *et al*.[52] analyzed the influence of temperature in the range of 20°C to 40°C on the yield of BC produced in the Hestrin-Schram medium (HS) and verified that the ideal temperature would be 30°C, concluding that the temperature affects not only productivity but also morphology and crystalline structure of the final biopolymer. In addition, they found that by decreasing the culture temperature from 30°C to 25°C, there was no significant decrease in BC yield compared to the variation from 35°C to 30°C. Identical results were found by Erbas *et al*.[53], Zeng *et al*.[54], Pecoraro *et al*.[23], and Hungund and Gupta.[50] Already Hirai *et al*.[55], showed that the CB produced by *the bacterium A. hansenii* ATCC 23769 in HS medium at 40°C and formed by cellulose bands II, while the BC produced at 28°C led to a morphology formed by cellulose strips I.

Media with different initial pH conditions tend to have different responses regarding the production of CB, because the variation of pH in fermentation processes can cause an increase or decrease in sugar consumption, consequently affecting the cell division and the number of nutrients available in the medium. The optimum pH for bacterial cellulose production is dependent on the microorganism that will be used, varying the pH from 4 to 7.[56] According to studies conducted by Son *et al*.[52], The production of BC was observed in the pH range of the medium from 4.5 to 7.5, leading to a higher production of BC at pH 6.5. Similar results were found by Yassine *et al*.[57] Already Panesar *et al*.[56] tested an industrial production of BC for biomedical applications, at pH between 4 and 4.5, to avoid contamination of the medium during cultivation. It is important to emphasize that the use of buffer is interesting to avoid the fall of

the pH during the fermentation process being necessary to obtain a higher yield.[40] This decrease in pH occurs mainly when glucose is used as a carbon source, and it is important to control it within the optimal pH value range.[58,59]

This parameter is essential to analyze cell metabolism, which interferes in increasing the yield of BC production, as well as in the final quality of biopolymer. It is worth mentioning that high concentrations of dissolved oxygen can increase the rates of gluconic acid, which confers cellular infeasibility when synthesizing cellulose.[50,60]

BC can be grown both in a static and agitated medium. In an agitated medium, BC forms granules and still makes the medium viscous with the presence of cellulose in gelatinous structures. In a static medium, the biomembrane remains at the liquid-air interface forming a film, which its thickness increases according to the time of cultivation.[53]

Yan *et al*.[61] studied that the BC produced in an agitated medium has lower mechanical resistance when compared to that produced in a static medium.

Regarding the composition of the culture medium, studies have been reported on the ability of bacteria of the *genus Gluconacetobacter* to metabolize various carbon sources and consequently influence the production yield of BC, resulting from the composition, so the number of sugars available in the substrate becomes important for the metabolism of bacteria.[62-63]

According to reports in the literature, several sources of carbon (monosaccharides, disaccharides, oligosaccharides), alcohols (ethanol, glycerol, and ethylene glycol), organic acids (citrate, succinate, and glycolate), and other compounds have already been studied to maximize bacterial cellulose production.[49]

As already mentioned, the main BC production medium was reported by Hestrin-Schram[44], in which glucose and citric acid were used as a carbon source and yeast and peptone extract as nitrogen source. Such research to discover other low-cost and carbon sources that serve as a substrate *for G.xylinum* is very important for the viability of large-scale production of bacterial cellulose, which allows the substitution of plant cellulose by bacterial biopolymer.[64,65] However, some studies suggest the use of cheaper carbon sources, such as glycerol, maltose, xylose,

mannitol, and by-products from the agroindustry, to reduce production costs and increase yield, as 65% of the value of commercial pulp is related to the cost of production.[40,64]

Studies conducted by Jonas and Farah[66] reported the occurrence of an increase in CB production using D-arabitol of 6.2 times and with D-mannitol of 3.8 times compared to glucose. Castro *et al*.[67] verified the production of BC *by Gluconacetobacter*, using other sugars (maltose, cellobiose, xylose, sucrose, and galactose) in place of glucose in HS medium and observed that such sources did not provide higher production. In contrast, Hong and Chi[68] and Yodswan *et al*.[69] Using the Strain *G. xylinus*, considered that mannitol and fructose are the best carbon sources for BC production. Keshk and Sameshima[70] and Jung *et al*.[49], obtained a significant production only with the use of glucose, fructose, and glycerol, as carbon sources. Ramana *et al*.[71] reported that among the substrates of carbon, lactose, galactose, citric acid, starch, and maltose produced less than 2.0 $g.L^{-1}$ of cellulose.

Mikkelsen *et al*.[63] utilized sucrose as a carbon source, which presented a low yield in the first 46 hours of fermentation, after 96 hours high yields were observed. But Zhong *et al*.[71], used six sources of carbon, glucose, mannitol, glycerol, fructose, sucrose, and galactose; and observed that more than 96 h of the use of glycerol and glucose provided better production yields compared to the other sources, without presenting differences in structural characterization. Kesh and Sameshima[73] evaluated cellulose production by G. xylinus from 18 carbon sources, among which only fructose and glycerol presented cellulose yields close to glucose, and glycerol was 55% higher.

Some authors report that the BC crystalline index is affected by the change in nitrogen and carbon source.[51,63,70] Jung *et al*.[49] also state, in their studies, that the amount of sugar can influence the osmotic effect, because the high concentration of sugars can promote a lower level of water activity by decreasing the metabolic rate and, consequently, the synthesis of BC. On the other hand, yeast extract is the most complete nitrogen source for *Gluconacetobacter species*, as it provides an adequate amount of nitrogen and growth factors for the strains.

In addition to the main sources of carbon, nitrogen, and phosphorus, culture media should contain elements in a smaller amount, called Trace elements, such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+},

and among others, which play an important role as enzymatic cofactors in polysaccharide production pathways.[63,70]

Therefore, determining an ideal environment and the right growth conditions to enable high levels of pulp production will add the characteristics needed to extend the technology to the industrial field.[51]

Bacterial Cellulose in The Generation of Adsorbent Matrices

Due to the advance in technology and the increase in the life expectancy of the population, industrial and agricultural fields have advanced a lot in recent years, as well as family activities, resulting in the insertion of various pollutants in the environment, especially in the soil and in the aquatic environment. Among these pollutants are organic substances, inorganic anions, metal ions, and micropollutants. To eliminate this large number of pollutants, and due to their different structural matrices; various techniques are adopted.[74] In the last 10 years, some researchers have pointed out that the adsorption technique has great potential to remove pollutants, indicating new research using pure or modified cellulose (composites) with the adsorbent matrix.

In this context, much scientific research has focused on the development of the ideal engineering for the production of BC-based products.[72] However, because it has a porous nature due to the distribution of the fibers in its composition, it makes it possible to add several materials to the cellulosic matrix. Thus, the composites are composed of two distinct materials, the matrix and the reinforcing material, where the matrix acts as a support to the reinforcing material, thus providing even more significant physical-chemical and biological properties to the biopolymer.[75]

BC modifications can be obtained based on the type of technique. Studies have shown that several compounds have been successfully added *to BC through in situ modifications*, when insertion occurs during the cultivation of the bacterium, the compound is diffused from the culture medium to the fibers. On the other hand, the ex *situ method* consists of the addition of the compound after the formation of purified BC.[15,76]

The *ex situ method* can occur by chemical or physical processes. The high number of hydroxyl functional groups present in the polymer chain allows a wide variety of chemical modifications by esterification reactions, esterification, halogenation, oxidation, chemical treatment, and

silylation.[77-78] On the other hand, chemical modifications include coating and adsorption processes.[75-76,79-80]

The adsorption process is a wastewater treatment method that has stood out because it presents an effective removal of organic and inorganic compounds. In turn, it is a technique that refers to a process where some of the chemical species of the fluid phase (adsorbate) adhere to the surface of the solid phase of a material (adsorbent), which can also be classified according to the type of adsorption, being them, physical (physisorption) or chemical (chemisorption).[81]

According to Miyashiro *et al.*[82], physical adsorption (fistulation) is characterized by van der Waals interactions, hydrogen bonds and induced dipole-dipole interactions, in which there is the addition of a monolayer of the compound that overlaps the adsorbent surface, being a reversible phenomenon, a relationship of intermolecular forces and weak attraction between the surface of the material and the adsorbate. The authors also note that chemical adsorption (chemisorption) is characterized by covalent or ionic interactions, being an irreversible process, because it is difficult to remove chemically absorbed species.

Cellulose-based products can be used in various separation technologies, namely in the commercial area, food and beverages, pharmaceuticals, scientific research, wastewater treatments, and others. In the treatment of contaminated environments, ethers and cellulose esters are the most used today, as they can perform all types of filtrations, due to their good adsorption capacity and toxic metals and other pollutants. [83] Pure cellulose has adsorption properties, but when chemically modified it has a higher adsorption capacity for various contaminants.[74]

Applications of Nanomaterials Containing CB Matrices for Adsorptive Processes in Contaminated Environments

In the literature, a diversity of compounds can be found that can be added to the bacterial cellulosic matrix to evaluate changes in morphology, yields, and crystallines and produce different composites that are applied in adsorptive processes for the removal of contaminants.

Stoica-Guzun *et al.*[84] synthesized a composite of bacterial-magnetite cellulose, in which the experimental data obtained proved that the nanocomposite can be used to remove chromium ions (IV) from wastewater at pH 4, with a minimal dissolution of magnetite during operation.

Zhuang and Wang[85] studied BC modified with nickel hexacyanoferrate (Ni-HCF) and found that the maximum adsorption capacity of Cesium ions (I) was approximately 175.44 $mg.g^{-1}$ at pH 6, indicating an efficient adsorbent for cs^{+} removal, where the mechanism is performed through ion-exchange between monovalent cations presented in the modified cellulosic network was responsible for capturing Cs^{+}.

Jin*et al.*[86] modified bacterial cellulose with polyethyleneimine and obtained a maximum adsorption capacity of copper (II) and lead ions (II), respectively 148 $mg.g^{-1}$ and 141 $mg.g^{-1}$, presenting a higher absorption compared to unmodified BC. However, the effect of pH directly affects the process of adsorption of metal ions, as they observed precipitations in the Solution of $CuSO_4$ when the pH was higher than 5.5, as well as in the solution of $PbCl_2$ when the pH was higher than 6.3. Thus, it was observed that Cu adsorption (II) was performed at pH 4.5 while Pb (II) reaches its capacity at pH 5.5. Kumar and Sharma[87], on the other hand, developed bacterial cellulose functionalized with N-isopropilacrilamide and acrylic acid, for Ni(II), Cu(II), and Pb(II) and ion adsorption tests, in which a maximum adsorption capacity of Ni(II), Cu(II) and Pb(II) ions were verified, were 79.78 $mg.g^{-1}$, 84.67 $mg.g^{-1}$ and 118 $mg.g^{-1}$, respectively at pH 5.

Shen *et al.*[88], in turn, synthesized the biosorbent by modifying bacterial cellulose with diethylnotamycin and verified that the best composite adsorption performance for Cu (II) and Pb (II) ions was obtained in a solution with pH 4.5, reaching its maximum adsorption capacity of Cu (II) and Pb (II) of 63.09 $mg.g^{-1}$ and 87.41 $mg.g^{-1}$, respectively, providing relatively comprehensive data for the application of modified biomaterial in the removal of metal ions in wastewater. Chen *et al.*[89], synthesized carboxymethyl bacterial cellulose, and verified a good adsorption performance at pH 4.5, with a maximum adsorption capacity of Cu ions (II) of 12.53 mg.g-1 and Pb (II) of 60.42 $mg.g^{-1}$.

In this way, Zhang *et al.*[90] synthesized hydroxypropyl cellulose xanthate and observed that at pH 5 the maximum adsorption capacity of Cu ions (II) was 126.58 $mg.g^{-1}$, while at pH 6 the adsorption capacity of Ni ions (II) was 114.24$mg.g^{-1}$, the mechanism involved in adsorption of these ions results in ion exchange followed by complexation. The composite binds transition metal ions by forming the coordination complex in which four sulfur atoms or two sulfur atoms are associated with a divalent metal ion.

CONCLUSION

Although plant pulp is very versatile, sustainability and environmental protection lead people to seek alternative materials. Among them, bacterial cellulose stands out, a material that presents fibers on a nanoscale, against the micrometric of plant cellulose, besides presenting excellent properties when compared to vegetable cellulose.

The present work sought to present the concept, properties, production, and chemical modifications of bacterial cellulose to the reader, as well as to bring what has been most current in research on this biopolymer applied to the process of adsorption of pollutants in contaminated environments.

Bacterial cellulose, therefore, proved to be an excellent adsorption matrix, and modified bacterial celluloses have more active sites that allow interaction with metal ions, thus being considered efficient methods of removal allowing experimental studies of these systems with environmental applications.

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