Algal Biopolymers

Subjects: Materials Science, Biomaterials

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Algae can produce a broad variety of biopolymers. Algae are diverse photosynthetic organisms that can be classified into various groups, including green algae, red algae, and brown algae. Algal biopolymers can be extracted from different parts of algae, such as the cell walls or intracellular compartments.

Keywords: microalgal biofuel ; algae-based biopolymers ; bacterial biopolymers

1. Different Algal Biopolymers

Algae can produce a broad variety of biopolymers. Algae are diverse photosynthetic organisms that can be classified into various groups, including green algae, red algae, and brown algae. Algal biopolymers can be extracted from different parts of algae, such as the cell walls or intracellular compartments. These biopolymers possess unique properties that make them suitable for various applications in industries such as food, pharmaceuticals, biotechnology, and materials science. Microalgae can produce polyhydroxyalkanoates (PHAs), proteins, and polysaccharides ^[1].

PHAs consist of repeated ester units with a carbon chain that is connected to two oxygen atoms and an R-group and can be subdivided into short, medium, and long chain length PHAs ^[2]. Mechanically, they can have thermoplastic and elastomeric properties, are stable in air, and have low water solubility, but are easily dissolved in many other solvents ^[1]. They are often biocompatible and biodegradable and thus used in many biotechnological and biomedical applications ^[3] ^[4].

Proteins consist of amino acids bonded by amide linkages, for building polypeptide chains $^{[\underline{1}]}$. Proteins are mainly used for food and thus to a lesser degree for bioplastic production. Investigations of algal proteins for bioplastic production were often carried out by blending the proteins as well as by comparing proteins received from different microalgae $^{[\underline{5}][\underline{6}][\underline{7}]}$.

Cellulose is a biodegradable polysaccharide from D-glucose monomers with glycosidic bonds, but has other linkages and a rigid, elongated structure ^[8]. It can be found in algal cell walls ^[8] with different amounts and different crystallinities, depending on the algal species ^{[9][10][11]}. Cellulose is often used in composites to reduce its low thermal stability and high moisture absorption ^[8].

Starch is also a biodegradable polysaccharide from D-glucose monomers with glycosidic bonds, forming a helical structure ^[1]. Depending on the ratio of amylopectin to amylose, its mechanical properties vary ^[12]. Starch can be converted to monomers used in polymer synthesis, be a part of low-molecular-weight polymers, or be a filler in other polymers ^[13].

It should be mentioned that other biopolymers, such as poly(lactic acid) (PLA), can be produced from carbohydrates, which can be obtained from microalgae ^[14].

On the other hand, macroalgae, also called seaweed, can be used to produce the polysaccharides, i.e., alginic acid and carrageenan, from which bio-based plastics can be prepared [I]. Alginate is a linear copolymer of mannuronic acid and guluronic acid bonded by glycosidic linkages, with the varying blocks of these acids resulting in different physical and chemical properties [15]. While alginate is derived from brown algae, carrageenan is mostly extracted from red algae. This polysaccharide consists of D-galactose and 3,6-anhydro-D-galactose, similar to agarose, which is also derived from seaweed [16].

2. Algal Biopolymer Production

As mentioned before, the main reason to switch from well-known and well-suited oil-based polymers to biopolymers is the increased sustainability of the latter. Nevertheless, it is necessary to keep their whole life cycle in mind, regarding carbon

footprint and the necessary energy to produce the required biopolymers. Algae biopolymers were shown to be advantageous in terms of biological composting and carbon sequestration as well as not using arable land [17]. One possibility to further reduce the ecological impact, which is often explored, is microalgae cultivation in wastewater, where wastewater treatment and biopolymer production are combined ^{[18][19][20][21]}.

Some of the commonly used microalgae are *Nannochloropsis* sp., *Botryococcus braunii*, *Spirulina* sp., and *Chlorella* sp., while typical seaweeds from which biopolymers are obtained are *Ulva prolifera*, *Ecklonia radiate*, *Undaria pinnatifida*, etc. ^[22]. Common biopolymer production routes are the fermentation of algal biomass by microorganisms, biopolymer production inside the algal biomass, or blending algal biomass with additives ^[22]. Amongst these routes, the zero-waste concept would include directly converting algal biopolymers, while the conversion to monomers as bioplastic precursor offers a broader range of producible biopolymers ^[23].

The large-scale commercial production of biopolymers can be performed in open or closed systems, with open systems having lower costs and larger production capacities but also higher contamination risks ^[24]. These non-standardized production methods, together with the broad range of algae used for biopolymer production and different production routes, reduces the reproducibility of the physical and chemical properties of the obtained biopolymers and thus should be optimized ^[25]. Besides extracting new polymers, this is why several researchers compared different biopolymers, obtained from various algal strands, and optimized algae cultivation and the subsequent biopolymer production ^{[26][27][28][29]}, e.g., by adding chemicals to modify the texture of alginate polymers ^[26].

3. Typical Applications of Algal Biopolymers

Algal biopolymers, especially from seaweed, are often used as food since they are abundant and sometimes especially healthy ^{[30][31][32]}. On the other hand, they can be used for food packaging due to their nontoxicity and biodegradability ^[33] ^{[34][35]}.

In addition, the specific physical and chemical properties of algal biopolymers make them suitable for different biomedical applications ^[36], such as nanocarriers for drug release in anticancer treatments ^[37] and wound dressings ^[38] or the well-known agarose gels for bacterial cultures and electrophoresis ^[36].

Other potential applications are related to fuel cells for wastewater cleaning [39] and energy harvesting and storage, as described in the next Sections. It should be mentioned that, depending on the planned application, the functionalization of the algal biopolymers is necessary, e.g., by crosslinking, by oxidation or substitution of functional groups, to reach the required physical and chemical properties [40]. On the other hand, specific processing techniques may support some applications, such as 3D printing, which has been investigated for algal polysaccharides by several research groups [41]. A more detailed description of some typical application areas is provided below.

3.1. Applications of Algae-Based Biopolymers for Food

Algae-derived carrageenan in food and beverage industry

Carrageenan, a polysaccharide extracted from certain species of red algae, is extensively used as thickener and stabilizer in various food and beverage products. It enhances the texture, viscosity, and palatability of food products in dairy products, desserts, beverages, and also processed meats. Algae-derived carrageenan is natural, plant-based, and hence vegan-friendly, meeting the growing consumer demand for clean-label ingredients ^[42].

Algae-based agarose as a gelling agent

Agarose, a polysaccharide derived from seaweed red algae, is generally used as a gelling agent in food and beverage products. It forms stable gels even at considerably low concentrations, making it ideal for confectioneries, desserts, and microbiological culture media. Algae-derived agarose is vegetarian-friendly and allergen-free and possesses excellent gel strength and clarity, making it a strong alternative for synthetic or animal-derived alternatives ^[43].

Algae-based biopolymer films for food packaging

Algae-derived biopolymers, like alginate and ulvan, are currently researched for their potential application in natural and biodegradable food packaging materials. These biopolymer films are also flexible, and possess good barrier properties against moisture and oxygen, making them suitable for extending the shelf-life of perishable food products. Introducing algae-based biopolymers for food packaging meets the increasing demand for eco-friendly alternatives to reduce plastic waste and environmental pollution ^[44].

3.2. Applications of Algae-Based Biopolymers in Pharmaceutics

Algal polysaccharides in drug delivery systems

Algal polysaccharides, like carrageenan and alginate, have been widely studied for their applications in drug delivery systems due to their advantageous properties of biocompatibility and biodegradability and also mucoadhesive properties. These polysaccharides can be formulated into different drug delivery systems, such as nanoparticles, hydrogels, and microparticles for controlled and targeted drug release ^[45].

Chitosan from algal sources in wound healing

Chitosan, a biopolymer derived from chitin, has been utilized in wound healing applications due to its antimicrobial properties, biocompatibility, and ability of promoting tissue regeneration. Chitosan derived from algae is advantageous due to its sustainable and renewable source compared to that of traditional crustacean-derived chitosan. Alginate-chitosan composite dressings have been developed for wound management, demonstrating enhanced healing properties [46].

Algal polysaccharides as anticancer agents

Algal polysaccharides, such as fucoidan and ulvan, are rapidly gaining attention for their potential anticancer properties. These biopolymers have demonstrated anti-proliferative, anti-metastatic, and immunomodulatory effects against various cancer cell lines. Fucoidan, in particular, has shown potential in inhibiting tumor growth and metastasis through multiple mechanisms, including the induction of apoptosis and the suppression of angiogenesis ^[47].

3.3. Applications of Algae-Based Biopolymers in Biotechnology and Tissue Engineering

Alginate

Alginate, a polysaccharide extracted from brown algae, has been extensively applied in biotechnology and tissue engineering for its ability to form hydrogels and its biocompatibility. Alginate hydrogels are being employed as scaffolds for tissue engineering applications due to their ability to support cell growth and mimic the extracellular matrix (ECM) environment ^[48].

Carrageenan

Carrageenan, a polysaccharide derived from red algae, has shown promise as a scaffold material in tissue engineering. Carrageenan-based hydrogels are being employed for wound healing and drug delivery due to their biocompatibility and ability to form stable hydrogel networks ^[49].

Ulvan

Ulvan, a sulfated polysaccharide extracted from green algae, has gained attention in biotechnology and tissue engineering for its unique properties of biocompatibility, biodegradability, and ability to stimulate cell proliferation and tissue regeneration. Ulvan-based hydrogels have been investigated for applications such as controlled drug delivery and wound healing $\frac{[50]}{2}$.

3.4. Applications of Algae-Based Biopolymers in Cosmetics

Alginate

Alginate, a polysaccharide derived from brown seaweeds, such as *Laminaria* and *Macrocystis* species, is widely employed in cosmetics for its ability to form hydrogels and films, imparting moisturizing and emulsifying properties to skincare formulations. Alginate-based masks, creams, and serums are popular in the cosmetics industry due to their hydrating and soothing effects on the skin ^[51].

Carrageenan

Carrageenan, a sulfated polysaccharide extracted from red seaweeds, including *Kappaphycus* and *Eucheuma* species, is employed as a thickening and stabilizing agent in cosmetics such as various skincare and haircare products. Its film-forming properties contribute to the texture and viscosity of cosmetic formulations, enhancing their spreadability and shelf stability ^[52].

Spirulina extract

Spirulina is a blue-green microalga rich in proteins, vitamins, minerals, and antioxidants. Extracts from *Spirulina* are increasingly utilized in cosmetics for their anti-aging, antioxidant, and skin-nourishing properties. *Spirulina* extracts are incorporated into various skincare products, including facial masks, creams, and serums, to promote skin hydration, elasticity, and rejuvenation ^[53].

3.5. Applications of Algae-Based Biopolymers in Biofuels

Algal lipids as feedstock for biofuel production

Algal lipids, particularly triglycerides, are a valuable feedstock for biofuel production due to their high lipid content and potential for conversion into biodiesel. Microalgae can accumulate lipids under specific growth conditions, making them a promising source for sustainable biofuel production ^[54].

Algal polysaccharides for bioethanol production

Polysaccharides extracted from algae, such as cellulose and starch-like compounds, can be enzymatically hydrolyzed into fermentable sugars, which can then be utilized for bioethanol production. Algal polysaccharides are advantageous due to the rapid growth, high carbohydrate content, and minimal land requirements of algae, making them promising feedstocks for sustainable bioethanol production ^[55].

Algae-based hydrocarbons for biofuel synthesis

Some algae species have the capability to produce hydrocarbons, such as alkanes and alkenes, which serve as precursors for renewable biofuels. These hydrocarbons can be extracted from algae biomass and can be further processed into drop-in biofuels with properties similar to petroleum-derived fuels ^[56].

3.6. Environmental Applications of Algae-Based Biopolymers

Algal polysaccharides for heavy metal remediation

Algal polysaccharides, such as alginate and carrageenan, have been studied for their potential in heavy metal remediation from various water bodies. These biopolymers can form complexes with heavy metal ions, facilitating their removal through precipitation or adsorption processes. Research has demonstrated the effectiveness of algal polysaccharides in removing heavy metals like lead, cadmium, and copper from contaminated water, providing a sustainable and eco-friendly approach to water remediation [57].

Algal biopolymer-based membranes for wastewater treatment

Algal biopolymers have been investigated as membrane materials for wastewater treatment applications due to their biocompatibility, biodegradability, and low-cost fabrication. These membranes can effectively separate pollutants from water using ultrafiltration, nanofiltration, and reverse osmosis. Studies have shown that membranes fabricated from algal biopolymers exhibit high permeability, selectivity, and fouling resistance, making them attractive candidates for sustainable wastewater treatment systems ^[58].

Algae-based biopolymers for soil stabilization

Algae-based biopolymers have been examined for their potential in soil stabilization and erosion control applications. These biopolymers, when applied to soil surfaces, can form a protective layer that helps prevent soil erosion caused by wind and water. Research has demonstrated the effectiveness of algae-based biopolymers in improving soil structure, reducing sediment runoff, and enhancing vegetation growth in degraded ecosystems. This application offers a sustainable and environmentally friendly solution to soil erosion and land degradation issues ^[59].

3.7. Applications of Algae-Based Biopolymers in Medical Devices

Alginate hydrogel

Alginate, derived from algae, has been widely used in the fabrication of hydrogels for various medical applications, including tissue engineering and drug delivery systems. Alginate hydrogels possess biocompatibility and tunable mechanical properties suitable for different tissue types ^[60].

Carrageenan-based wound dressings

Carrageenan, a polysaccharide extracted from red algae, has been applied in the development of wound dressings due to its biocompatibility, biodegradability, and ability to promote wound healing. Carrageenan-based dressings offer a moist environment for wound healing and can release therapeutic agents to aid wound recovery ^[61].

Spirulina-based scaffolds

Spirulina, a type of microalgae, has been employed in the fabrication of scaffolds for tissue engineering applications. *Spirulina*-based scaffolds offer benefits such as high porosity, biocompatibility, and the presence of bioactive compounds that can enhance cell proliferation and differentiation ^[62].

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