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Biopolymers Production from Algal Biomass and their Applications- A Review

Aluru Ranganadha Reddy*

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Abstract

Interesting properties like renewability, biocompatibility, and biodegradability are present in favorable materials produced by living organisms called biopolymers. They have recently caused some environmental concerns as they have been considered to compete with polymeric materials that are fossil-based. Energy, medical devices, electronics, and food packaging are some of the applications of biobased plastics that are gaining increasing interest. Microbes, agricultural wastes, animals, and plants are some examples of biological sources that can produce biopolymers. Among the promising sources for producing bioplastics are microalgae and cyanobacteria, both of which contain cellulose, carbohydrates (especially starch), proteins, and polyhydroxyalkanoates (PHAs), according to some studies. The potential of microalgal PHAs, polysaccharides, and proteins for the production of bioplastics is summarized in this review. A wide range of applications, including environmental remediation, adsorption, 3D printing, and antioxidants employ Biopolymers. A circular economy approach to microalgal-based bioplastic production is considered in this review to provide insight into current knowledge and future directions.

Keywords: Biopolymers, Microalgae, 3D Printing, Biomedical, Adsorbent

Introduction

The regular use of algae as a biomass feedstock has been made possible by quick improvements in the bioresource sector. Nearly fewer than 36,250 of the 72,500 identified algae strains have been examined, and their potential for a variety of uses is undeniable (Ali *et al*., 2021). Algae can produce a wide range of products, including carbohydrates, proteins, oils, polymers, and other bioproducts (Ranganadhareddy, 2022). Algae are an effective instrument for producing a variety of bioproducts due to their low cost and sustainability (Ranganadhareddy *et al.*, 2022). The algae's utility as a feedstock for various processes depends on the number of proteins, lipids, carbs, and fats it contains. Recent advancements have made it possible to combine bioproduct generation utilizing algal biomass with downstream processing. Biopolymers are widely used in cosmetics, medicines, and food packaging (Ranganadhareddy, 2022). Because of their great nutritional content, they are used as possible food ingredients (Bernaerts *et al*., 2019). The utilization of novel biopolymers, like chitosan, dramatically improves processes like medication delivery and tissue regeneration (Negm *et al*., 2020). Biopolymers and their composites are heavily utilized in contemporary technologies like 3D printing (Ranganadhareddy & Chandrsekhar, 2022).

Aluru Ranganadha Reddy*
Department of Biotechnology, VFSTR Deemed to be University, Guntur, India 522213.

***E-mail:** rangaaluri@gmail.com

The utilization of algae to create various biopolymers has seen several advances during the past few years. Starch and cellulose polymers are found naturally in algae and may be extracted from them using a variety of methods (Do Val Siqueira *et al.*, 2021). Algae are a significant feedstock for the manufacture of biopolymers due to their abundance of photosynthetic factories (Cheng *et al*., 2019). Polyesters, polyamides, polyolefins, and other polymeric classes can be produced by fermenting algal biomass (Yavari-Bafghi *et al*., 2019; Abdel-Latif *et al*., 2022). Natural polymers derived from algal biomass have potent anti-microbial, anti-tumor, antioxidant, and immunomodulatory properties while being less hazardous (Bilal *et al*., 2021). Algal biomass may also be utilized to create composites with high mechanical characteristics, such as adhesion and tensile strength, and that are biodegradable (Rai *et al*., 2021). This review examined the properties of algal biomass and its potential for producing biopolymers (Wei *et al*., 2020). The methods for producing biopolymers from algal biomass were discussed. A list of the several kinds of polymers made from algal biomass was provided, along with examples of how they may be used in biomedical, environmental, and mechanical domains. Future research requirements and prospective opportunities were identified in addition to the thorough evaluation.

Biopolymer Production with Algae as the Precursor

In the manufacturing of bioplastics, often *Spirulina* is used as feedstock. *Spirulina* is a spiral microalga that has a high protein content which can range from 46 to 63% by dry weight. The small round or oval cells that makeup microalgae have strong cell walls. These microalgae are cost-effective as their tiny cell size makes it so that they do not need extraction which is the main benefit of these microalgae. Lipids and chlorophyll are present in the algae attrace levels. The microalgae, *Spirulina* are generally used combined with other substances. *Spirulina platensis* and polyvinyl alcohol were shown to promote the development of composites, resulting in robust interactions and a composite with suitable tensile strength, according to Dianursanti *et al.,* (2019). When compared to macroalgae, *Spirulina* has a higher content of carbon and nitrogen, being 46.9% wt% and 0.2 wt%, respectively. As the algae can endure high pH as well as saline environments, it acts as a promising feedstock for operations thatrequire conditions like that (Feng *et al*., 2018).

Biopolymers Produced from Algal Biomass

Polyhydroxtbutyratye

Poly-3-hydroxybutyrate-co-3-hydroxyvalerate is created when 3-hydroxyvalerate units are added, causing PHB's extremely crystalline structure to be broken. PHBV is a useful tool in drug delivery systems because of its exceptional physiochemical characteristics and slow rate of degradation (Ranganadha *et al.,* 2020). The manufacturing of PHBV and its uses in the biomedical industry have both been thoroughly investigated. The study also provided unique methods for developing novel structural systems based on PHBV. With the help of a recombinant *Bacillus megaterium* strain, PHBV could now be produced from glucose without the requirement for precursors. It can be shown that fed-batch culture increased total production compared to batch cultivation since over 80% of PHBV polymer was generated in the fed-batch technique as opposed to 46% in the batch method. Algae can be exploited as a source of glucose in the future, and a similar process might be employed commercially to create PHBV (Ranganadha & Chandrasekhar, 2021).

Polylactide

Many researchers are interested in polylactide because it holds great promise for biological applications such as sutures, braces, bandages, and bone screws. The effects of algae-PLA composites have been the subject of several investigations. Algae's chemical makeup may be changed to create PLA-biomaterials that can be used for tissue augmentation, wound healing, and tissue regeneration (Sayin *et al.,* 2020). Comparatively speaking, poly-alcohols are more biodegradable, water-soluble, and have better tensile strength. Recently, they have been widely used to create bio-composites for a range of purposes. Polyvinyl alcohols (PVA) are polyalcohols used as emulsifiers, sizing agents, and protective coatings. Innovative material compositions might be made using biocomposite PVAs. Lipid Extracted Algae was looked at as filler for the PVA-based biocomposite synthesis. Algal loading reduces the mechanical properties of a composite while increasing its thermal stability. Electrical, mechanical, and thermal properties can be considerably enhanced by using biocomposite polymers made of algae. The production of biopolymers frequently involves processes like electrospinning, melt casting, and others. Algae-polymer composites are a potential choice in biomedical applications due to their low-cost efficiency and low risk of tissue harm (Reddy *et al*., 2017).

Biopolymers from Algal Biomass

Biopolymers can be generated from algal biomass in three ways, as shown in **Figure 1**. First, biopolymeric chemicals are produced by microorganisms fermenting algal biomass; second, natural biopolymers are produced by cell factories inside algal biomass; and third, composite algal biopolymers are produced by mixing algal biomass with additives (3rd route). In the fermentation process, enzymes produced by algae are used to convert algal biomass into bioproducts that contain biopolymers (Suparmaniam *et al*., 2019). Recent research has focused on the fragmentation of algal biomass and the extraction of vital lipids, proteins, and carbohydrates before the fermentation process.

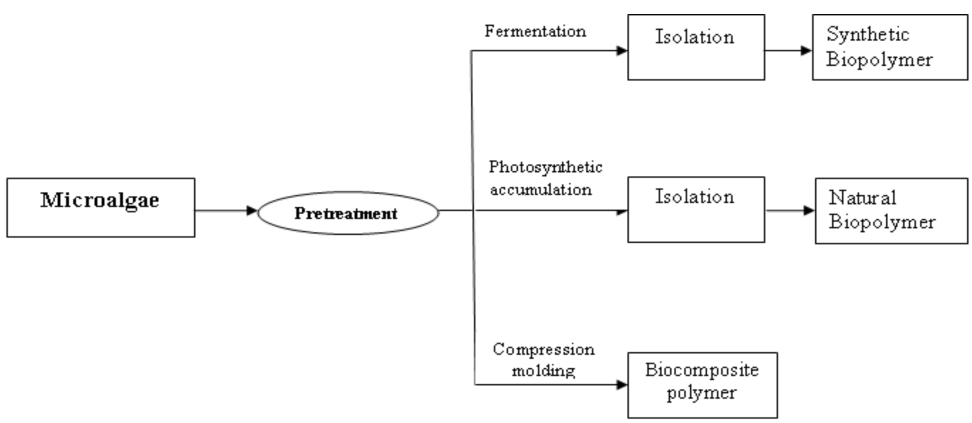

Figure 1. Biopolymer synthesis from microalgae (Kartik *et al*., 2021)

In a novel subcritical hydrothermal method, Steinbruch *et al*., (2020) showed how algal biomass could be broken down with water and subsequently fermented to make PHA. However, PHA is shown in **Figure 2**. Recovered starch and cellulose yielded 5.1% and 3.1%, respectively, while PHA from untreated biomass yielded 77.8% mg/g (biomass). As a consequence, it was shown that immediately fermenting biomass as opposed to breaking it up into smaller bits is more economical. The second approach involves using a light source to create polymers inside the algal biomass during photosynthesis. Microalgae are a great option for the production of biopolymers since they only require small amounts of nutrients (Costa *et al*., 2018). Polysaccharides, lipids, and lignin, which are precursors for the synthesis of biopolymers, are examples of specific organic substances that might accumulate as a result of changes in light intensity and periodicity (Cassuriaga *et al*., 2018). As a consequence, for 6 hours, algae with xylose supplementation was exposed to light with an intensity of 28 mol m-2s 1.PHB was produced at a rate of 17.4% as a result of this. Adjusting exposure times and intensity may boost the formation of biopolymers. Gamma radiation, on the other hand, has recently been found to improve material properties while being both easy to utilize and environmentally friendly. For the creation of biopolymers, UV light may be employed. In the literature, Nasir and Othman (2019) developed a starch-based biopolymer using UV irradiation. Starch and UV-generated free radicals interact to form crosslink chains. As a consequence, one may construct and create biopolymers with the necessary properties utilizing UV. Algae-polymer combinations are created using the third technique. The most common method for creating biocomposite involves compressing algae and chemicals while holding them in a mould (Ciapponi *et al*., 2019). Another popular technique is solvent casting, which involves dissolving additives and algae in a solvent and then drying the mixture on surfaces to create films. By mixing the components on a glass plate and air drying it for 24 hours to produce biopolymeric films, Park and Lee, (2022) produced polyvinyl alcohol (PVA)-algae. Onen Cinar *et al.*, (2020) have provided a thorough description of the procedures used to create blends of algae and polymers as well as the testing procedures used to evaluate the properties of composite polymers.

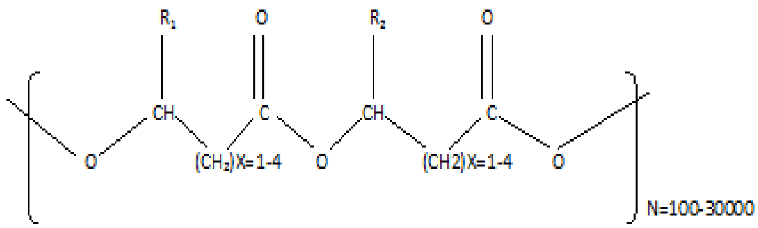

Figure 2. Polyhydroxyalkanoates with R_1 and R_2 are alkyl groups (C-C)

PHA made from microorganisms is safe for the environment and resembles petrochemical polymers in its properties. Stress brought on by a lack of nitrogen can hasten the production of biopolymers. *Chlorella minutissima* did not synthesize PHA biopolymers, even in the presence of a nitrogen deficiency, unlike *Synechococcussubsalsus* and *Spirulina*. The majority of the PHA monomer composition depends on the microbial strains and culture strains. All lab-scale experiments are still in the process of scaling up bioprocesses, which calls for a lot of attention. A Mixed Integer Nonlinear Programming approach was suggested by Ramos *et al.* (2019) to enhance PHA manufacturing plant conformation. They maximize the net present value of the plant and identify the ideal circumstances for the facility. Additionally, they can help decide between many options for extracting biopolymers from cells and choosing the optimal strategy to extract the greatest quantity of biopolymers.

PHB is an optically active, biodegradable, apolar polymer that has attracted a lot of attention due to its similarities to polypropylene. Compared to lignocellulosic biomasses, starch-rich biomasses produce more PHB. The usage of algae as a precursor in the production of PHB is not well understood. The production of PHB requires a lot of lipids. Generally speaking, delayed cell growth causes a significant accumulation of lipids for the formation of biopolymers. The impact of environmental factors on *Chorella fuscas* PHB production was examined by Cassuriaga *et al*. (2018). The highest amount of PHB (17.4%) was found during their experiment, surpassing the PHB production seen in *Botryococcusbraunii* as shown by Lozoya-Gloria *et al.* (2019) recently, research on PHB generation from agricultural runoffs has been conducted. The complete capability of bacterial PHB production was shown, notwithstanding the low PHB concentrations that were attained. Algae productivity and PHB accumulation characteristics may also be optimized to develop a workable manufacturing method.

Applications

Adsorbent

Adsorption produced by the use of biological molecules is powerful and effective and doesn't result in any secondary pollution. It is also very simple to recover and reuse (Upadhyay *et al*., 2021). Clays and biopolymers work together in an adsorption process to remove colors and remediate heavy metal contamination. Hydrophobic contaminants cannot be removed by using natural clays; instead, biopolymers such as polysaccharides and polypeptides are employed. This results in a fruitful combination that may be applied to environmental cleanup (del Mar Orta *et al.*, 2020). When clay and biopolymer are combined as biocomposites, their qualities, such as resilience to pH fluctuations, low wettability, and poor specificity, significantly improve compared to when they are used individually.

According to Xia *et al.* (2020), two bacterial strains from wastewater treatment plants *Klebsiella* and *Bacillus* sp. were used to remove mercury. For the elimination of organic pollutants, a biopolymer with integrated phosphate groups (Pcel) has been developed. Utilizing sodium tripolyphosphate and phosphoric acid, cellulose's surface is modified to create the biopolymer. The highest levels of adsorption for both organic pollutants were at acidic to neutral pH, with a capacity of 47.58 mg/g for Rhodamine B and 45.52 mg/g for Amitriptyline (Kassiri *et al*., 2020). Due to its benefits and quantity, as well as the ease with which its surface may be altered by the interaction of hydroxyl (OH) groups, modified cellulose is frequently used in investigations as a material for adsorption.

Biomedical Field

Due to theirbeneficial qualities including biodegradability, non-toxicity, high tensile strength, and water-holding capacity, biopolymers are also employed in the biomedical engineering sector, particularly in the development of regeneration medicines and bone tissue engineering (Lippi & Plebani, 2020; Ranganadha & Chandrasekhar, 2021). The production of hydroxyapatite (Hap) composite biopolymer from chitosan is discussed in a recent work published in Sathiya-Vimal *et al*., (2020). Since Hap is a crucial mineral for human bone. Soybean oil epoxidized acetate (SOEA) and Hap nanoparticles are used by Bahmani *et al.* (2019). The mechanical characteristics of the biopolymer were examined after hydroxyethyl acrylate was introduced to one portion of the composite and not to another. Marine algae-PLA composites for collagen membranes were investigated by Sayin *et al.,* (2020). In this study, polylactide was used to improve the qualities of many algal strains, including *Corallina elongata*, *Galaxia oblongata*, *Cystoseriacompressa*, *Sargassum vulgare*, and *Stypopodiumschimperi*. *Sargassum vulgare*, Type IV MAP, demonstrated the finest qualities for skin grafting applications out of all of them (Kardile & Shirsat, 2020).

3D Printing

Due to its ability to quickly and accurately build complicated structures, 3D printing has gained popularity recently. The challenge at this point is to describe the mechanical and biological characteristics of naturally existing bio-based materials (Chen *et al.,* 2022). Biopolymers are intensively explored for 3D printing technologies (Reddy *et al.,* 2019). Ponthier *et al*. (2020) fill PVA biocomposite for 3D printing with *Nannochloropsis salina* algae. Biopolymers may be used for a variety of applications that call for various material qualities thanks to their adaptability. Adsorption for environmental cleanup and biomedical applications uses 3D-printed biopolymers. Sangiorgi *et al.,* (2019) created fillers for the breakdown of methyl orange using polylactic acid modified with TiO_2. Methyl orange can degrade completely in 24 hours because of the composite's use of 30 wt percent TiO_2. The stem cell activity of 3D-printed scaffolds coated with nanoscale ceramics was investigated.

Conclusion

Algal biomass offers enormous potential for the manufacture of biopolymers, as was addressed in the review. The production process is, however, hampered by a few bottlenecks. Algal growth in photobioreactors demands significant expenditure for large-scale production. A sustainable method for growing algae on a big scale with lower production costs may be developed. There are problems with both the large-scale production of biopolymers and the disposal of wasted biomass. In this regard, models encouraging the bioeconomy might be developed using the concepts of the circular economy. Additionally, utilizing neural network optimization techniques, research may be done to establish the best ideal conditions for algae growth and bioreactor for fermentation. It is feasible to screen microalgal species to find the optimal algal biomass for the manufacture of biopolymers. The purpose of this review is to emphasize the significance of algal biomass and its value in the production of biopolymers. Furthermore, new advancements in biopolymer synthesis techniques using algal biomass were presented. The subject of biomedical sciences has a lot of potential for biopolymeric materials. Furthermore, molecular motors and artificial implants can be created with the use of 3D printing technology. The development process can be sped up by the biopolymeric materials utilized in 3D printing.

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