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A Review Study on the Potential of Microalgae Biomass Producing Biopolymer Material

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ABSTRACT – This review focuses on the potential of microalgae biomass in producing biopolymer materials. Microalgae have gained attention as a sustainable and renewable source of energy and other useful products such as biofuels, pharmaceuticals, and cosmetics. One promising application of microalgae is as a source of biopolymers, which can be used as a sustainable alternative to traditional petroleum-based plastics. The review is conducted through a comprehensive search of electronic databases, screening of relevant articles, and synthesis of information obtained from the selected studies. The review also critically evaluates the strengths and limitations of the existing research on the potential of microalgae biomass in producing biopolymer materials. The outcomes in this review highlights key findings related to the potential applications of microalgae biomass in producing biopolymers and identifies areas for future research. The conclusions and recommendations of this review are important for guiding the development of sustainable and environmentally friendly biopolymer materials.

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INTRODUCTION

The increasing level of carbon dioxide (CO_2) in the atmosphere is one of the major contributors to climate change, and this issue is strongly correlated with our dependence on fossil fuels. If this issue is left unresolved, it may reach a critical point beyond which our efforts to restore balance will become ineffective [1]. As we moved toward alternative sources of energy, there remains a necessity for high-energy-density fuels to replace petroleum. Liquid fuels derived from biomass represent one sustainable option and corn-based ethanol has led the way in providing a source of first-generation biofuel. However, in recent years corn-based ethanol has received criticism for its reliance on fossil fuel for production. Life cycle assessments indicate that corn-based ethanol would not qualify as an advanced biofuel, but one viable route to decrease the amount of CO_2 emitted from an ethanol biorefinery is through the co-cultivation of microalgae. Microalgae photo-bioreactor major challenge for harvesting is the handling of large volumes of cultivation water to concentrate low amounts of biomass. Although the main factors that consume energy and cost during lipid extraction involve breaking down the cell wall of algae and drying the biomass before extracting the lipids using solvents, the high amount of energy required to remove water from the plants in the initial stages of the process has made converting algae into biofuel and biopolymers impractical, inefficient, and uneconomical. Moreover, the increasing interest in reducing the use of petroleum-based plastics is a result of their significant negative impact on the environment. Petroleum-based plastics are not easily biodegradable and can persist in the environment for hundreds of years, leading to a build-up of plastic waste in landfills and oceans. This build-up of plastic waste has significant negative consequences, including harming marine life and contributing to the degradation of ecosystems. The staggering statistic that more than eight million tons of plastic waste leaks into the ocean every year underscores the urgent need for innovative approaches to redesign packaging materials to reduce plastic waste. There is significant interest to decrease the reliance on petroleum-based plastic products, which causes global environmental pollution [2]. More than eight million tons of plastic waste leaks into the ocean every year, which can be mitigated through innovative redesigns of packaging materials [3].

Biopolymers are a type of polymer produced from renewable resources like animals, plants, bacteria, fungi, and algae. The biopolymers have many potential applications in various fields. Among the renewable resources of biopolymers, algae are particularly promising organisms due to their ability to produce natural compounds through the process of algae photo-bioreactor. However, the accumulation of a large amount of polymer waste during this process poses a challenge that can be addressed by using biodegradable polymers. The justification and importance of studying biodegradable polymer by algae can be summarized as follows:

i. Environmental sustainability: Biodegradable polymers derived from algae can provide a more sustainable alternative to petroleum-based plastics, which have a significant negative impact on the environment.
ii. Resource efficiency: Algae can be grown using renewable resources like sunlight, water, and carbon dioxide, making them a more resource-efficient source of biopolymers than petroleum-based plastics.
iii. Economic potential: The development of biodegradable polymers derived from algae has the potential to create new economic opportunities in fields such as bioplastics, biomedicine, and agriculture.

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iv. Innovation and research: The study of biodegradable polymers derived from algae requires innovation and research, providing opportunities for scientific and technological advancement in the field.

v. Addressing global challenges: The problem of plastic waste and environmental pollution is a global challenge, and the development of biodegradable polymers derived from algae can contribute to solutions for this problem.

Overall, the study of biodegradable polymer by algae is important and justified because it can contribute to address important global challenges related to environmental sustainability and resource efficiency, while also providing economic potential and opportunities for scientific and technological advancement.

ECONOMICAL VALUES OF BIOPLASTIC OF MICROALGAE BIOMASS

Microalgae have the potential to be a superior biomass option for bioplastic production, as it doesn't compete with food sources and can thrive on waste materials while also having the ability to accumulate high levels of lipids. Nonetheless, microalgae can serve as a substitute for other sources in biofuel production, acts as a supplement in the food industry, cosmetics, and pharmaceuticals. The production of bioplastic using microalgae has gained popularity due to its potential contributions to the circular and bioeconomy, which can be more sustainable. Bioplastic made from microalgae has multiple applications, including in food packaging, pharmaceuticals, and cosmetics.

Bio-based plastics are further classified into three categories: Modified natural polymers, synthesized bio-based polymers from synthesized bio-based monomers and bioplastics from waste [4]. Currently, only around 1% of the annual plastic production in the world is bioplastics. In 2019, the market share for both non-biodegradable and biodegradable bio-based plastics was evaluated. The majority, constituting 21% of total production, was attributed to starch blends. There is an anticipated increase in the market share of bioplastics. The primary application areas for bioplastics are in the packaging industry, with the textile, automotive, and construction industries [5].

The market share of bioplastics is expected to increase due to several factors. First and foremost, there is a growing concern regarding the environmental impact of traditional plastics, which has led to an increasing demand for more sustainable and eco-friendly alternatives. Bioplastics are considered to be a more sustainable option as they are derived from renewable resources such as corn starch, sugarcane, or cellulose, and can be biodegradable, reducing the burden of waste accumulation.

Secondly, technological advancements have made bioplastic production more efficient and cost-effective, leading to increased adoption by manufacturers. Additionally, government policies and regulations have been put in place to encourage the use of bioplastics, such as bans on single-use plastics and incentives for using eco-friendly materials. Finally, as consumers become more aware of the impact of their choices on the environment, there has been a shift towards sustainable and responsible consumption. This has resulted in an increased demand for products made from bioplastics, particularly in the packaging industry, where consumers are actively seeking out products with eco-friendly packaging. These three factors are expected to drive the market share of bioplastics upwards in the coming years.

Plant-based raw materials, natural polymers such as carbohydrates and proteins, as well as small molecules like sugar, disaccharides, and fatty acids, can be used as sources for bioplastic production [5]. The production capacity for bioplastics has grown from roughly 2 million tons in 2014 to about 6.7 million tons in 2018, with starch and poly(lactic acid) (PLA)-based polymers being the most commonly used materials [5]. However, because of bioplastics are often derived from crops like corn and potatoes, it can compete with food supplies [1]. Additionally, the production of bioplastics from agricultural crops requires large land areas, water, and nutrients, making it unsustainable in the long term according to numerous studies. Moreover, the commercialization of bio-based compounds on a large scale has faced many challenges in the last decade.

When compared microalgae and agricultural crops as a source for bioplastics, the microalgae presents more sustainable option. Microalgae can be grown on non-arable land using waste resources such as carbon dioxide and wastewater, thereby avoiding competition with land and food sources [1]. Furthermore, microalgae have the ability to accumulate lipids and other organic compounds that can be used to produce bioplastics, making them a promising alternative to traditional sources such as corn and potatoes [2].

Despite the advantages of using microalgae as a source for bioplastics, there are still challenges that need to be addressed. One of the main challenges is that the high cost of producing microalgae at large scale, which is often due to the cost of inputs such as nutrients and energy. Additionally, the process of extracting and refining the organic compounds in the microalgae to be used in bioplastics can be a complex process and costly.

However, research and development activities are progressing to overcome these challenges and optimize the production of microalgae-based bioplastics. As the demand for sustainable alternatives to traditional plastics continues to grow, it is likely that microalgae-based bioplastics will play an increasingly important role in the bioeconomy.

MICROALGAE SPECIES PRODUCED BIOPLASTIC

Microalgae are microscopic organisms, which utilize solar energy to produce adenosine triphosphate and live in freshwater and marine environments [6]. Microalgae can replace many other sources for biofuel production, be used as supplements in the food industry, cosmetics and in pharmaceutical formulations. Microalgae is becoming increasingly popular due to its potential contribution to the bioeconomy. The common microalgae products are shown in Figure1.

Chlorella is a genus of green algae, which can be found in freshwater and contains around 58% (by weight) protein. It has higher crack resistance due to its dense cell walls and higher thermal stability compared to Spirulina [7]. This species is often used in biomass–polymer blends. According to Zeller et al. (2013), after comparing bioplastic production from 100% microalgae biomass and blends containing additives and polymers, it was found that blending is necessary for commercial applications [7]. A testing was conducted to measure product quality showed that higher quality bioplastic could be obtained using Chlorella Vulgaris compared to Spirulina. However, Spirulina has better blending properties compared to C. Vulgaris based on physicochemical features of the material [7].

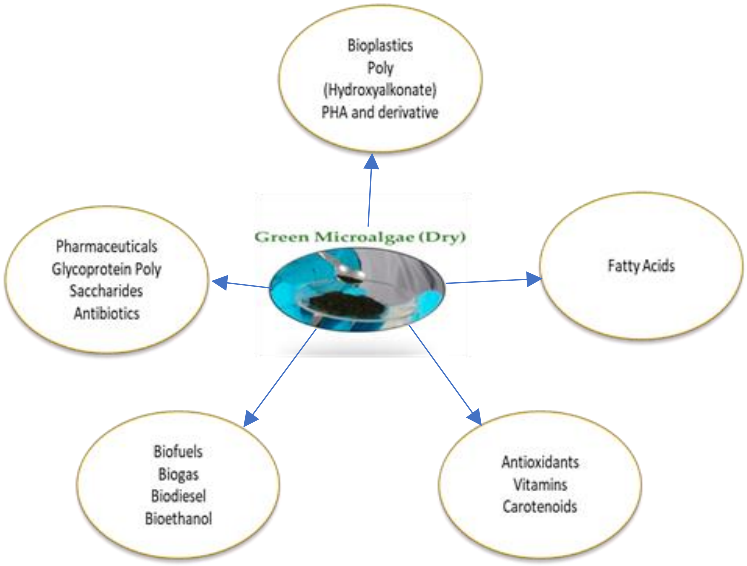

Figure 1. Common products of microalgae

Spirulina is a type of microalgae that has been found to contain various biopolymers, including polysaccharides, proteins, and polyesters, that can be used in the production of bioplastics [1]. The polysaccharides in Spirulina, such as carrageenan and agarose, have been found to exhibit gelling and thickening properties, making them useful in food and cosmetic industries. In addition, Spirulina proteins have shown potential in the development of biodegradable plastics with good mechanical properties. Spirulina, which is used for many years in the food industry as a protein source, is known for its adaptation potential for extreme environments [8]. Spirulina platensis contains a high concentration of protein. Its composition is shown in Table 1 [9]. When comparing Spirulina and Chlorella vulgaris, it should be noted that Spirulina has been more extensively studied for its biopolymer content and potential applications. Spirulina also has higher protein content compared to Chlorella vulgaris, which may make it a more attractive option for biopolymer production. Spirulina contains about 60-70% protein by dry weight, which is considered to be a high protein content. The protein in spirulina is also considered to be a complete protein, as it contains all essential amino acids that the body needs but cannot produce on its own. This makes spirulina a popular supplement among vegetarians and vegans who may have limited protein sources in their diets.

There have been several studies conducted to examine the potential of Spirulina for bioplastic production. Similar to Chlorella, Spirulina has a small cell size, which makes both of them attractive for bioplastic blend production. Despite their similarities, Chlorella and Spirulina showed different behaviors and bioplastic properties while blending with PE due to their varying amino acid contents.

Bacterial and algal cells produce polyesters of hydroxyalkanoates, known as PHAs, using sugar and/or lipids as an intracellular carbon source. PHAs possess similar physical properties to petrochemical-based plastics such as polypropylene, making them a suitable replacement for plastic bags and containers. The ester units in PHAs are comprised of a carbon chain bound to an R-group and two oxygen atoms. Several cyanobacteria species, including Calothrix scytonemicola, Spirulina spp., Aphanothece spp., Gloeothece spp., and Synechococcus spp., are known to produce P(3HB) using CO_2 as a carbon source (26). This is explaining that PHAs (polyesters of hydroxyalkanoates) are biodegradable plastics that can be produced by bacterial and algal cells using sugar and/or lipids as a carbon source. They can be used as substitutes for petrochemical-based plastics such as polypropylene, as they have similar physical properties. Certain cyanobacteria species, such as Calothrix scytonemicola, Spirulina spp., Aphanothece spp., Gloeothece spp., and Synechococcus spp., are known to produce P(3HB) (a type of PHA) using CO_2 as a carbon source.

For most organisms, including cyanobacteria, PHAs act as energy and carbon storage compounds Despite the low content of PHAs in microalgae, still far from the contents obtained with bacteria, the conversion of atmospheric CO_2 into PHAs without the use of a carbon source, which as mentioned before can account for a significant part of production costs, is very advantageous due to the necessity to compensate for the increasing emissions of CO_2. In addition, the utilization of microalgae in the production of PHAs is at a nascent stage in comparison to the processes employing bacteria, and the enhancement of the process is yet to be achieved. This is attributed to the distinctive features of PHAs, researchers and manufacturers intend to utilize these species of biopolymers in packaging, printing inks, coatings, laminations, waxes, binders, and adhesives [27]. Thus, and considering, for example, the high biocompatibility and sustainability associated with P(3HB), the number of companies producing these biopolymers is not surprising, namely the P(3HB) Industrial (Serrana, Brazil), Tianan (Ningbo, China), CJ CheilJedang (Dongho-ro, Korea)), Kaneka (Minato, Japan), and Biomer (Schwalbach am Taunus, Germany).

Table 1. Composition of *Spirulina platensis* [9]

Component	(wt%)
Protein	60
Lipid	6
Fattyacid	265 mg / 10 g
Aminoacid	2410 mg / 10 g
VitaminA	2300IU
VitaminB1-B3	2.3 mg / 10 g
Vitamin B6&B12	112 mcg
VitaminE	4IU
Phycocyanin	20%
Chlorophyll	1.5%
B-Carotenoids	0.15%
Pantothenicacid	4 mg·/ 100 g
Folicacid	100 mg·/ 100 g
Polysaccharide	0.4 g·/ 100 g

PRODUCT BLENDED WITH MICROALGAE BIOMASS

Studies on the production of bioplastic material from microalgae sources can be classified into two main approaches. The first approach is bioplastic which can be refered to composites produced by blending microalgae biomass, bio- or petroleum-based polymers and additives. The second approach is based on the cultivation of biopolymers such as polyhydroxybutyrates and starch intracellularly within microalgae cells. These products can be then extracted and further processed for bioplastic production. In this case, the microalgae cells are not utilized directly. Conventional polymers are commonly utilized to produce blended bioplastics from microalgae to achieve improved plastic properties [10,11,12]. Table 2 summarizes the research done in this area. PE and PP are the most used polymers in the blending process. They represent more than two-thirds of world plastic demand [13]. PE is consumed in a wide variety of industries such as cosmetics, food packaging, and medical products including prosthetics [14]. UHMW-PE is an extremely long chain PE that has a molecular weight between 2 and 6 million. Because of the PE is non-toxic and odourless with extremely low moisture absorption capacity, it is preferable for bioplastic production [15,16]. In the study conducted by Wang (2014), UHMW-PE at different ratios (20–80% at 15% intervals) were blended with Spirulina. Better tensile strengths were observed at the ratio 80:13:7 of PE-Spirulina-EG (Ethylene Glycol) [11].

Table 2. Blended materials with microalgae and used chemicals in the blending process.

Blended Materials with Biomass	Chemical Formula	Purpose of Usage	Reference
PE	$(C_2H_4)_n$	Blended with *Chlorella* and *Spirulina*	[17]
PP	$(C_3H_6)_n$	Blended with *Chlorella*	[18]
PVA	$(C_2H_4)_n$	Blended with *Chlorella*	[18]
Wheat gluten		Blended with *Spirulina* platensis	[19]
PBS	$(C_8H_{12}O_4)n$	Blended with *Spirulina*	[20]
UHMW-PE	C_2H_4	Blended with *Spirulina*	[11]
PVA-g-MAH (maleic anhydride-grafted PVA)		Used in blending process	[18]
Acetone	C_3H_6O	Used in blending process	[21]
Sodium sulfite	Na_2SO_3	Used in blending process	[22]
BPO	$C_{14}H_{10}O_4$	Used in blending process	[23]

On the other hand, since PP has a semi-transparent appearance and is resistant to heat and mechanical effects, it is preferred for the production of yoghurt, medicine, and beverage packaging [24]. In one study, PVA was used to create bioplastic films with Chlorella at different solution temperatures. The study revealed that elevated temperatures led to decreased bonding between the blended materials, and ultrasonication was found to enhance the quality of the resulting blend due to its impact on the mixture's homogeneity [25]. Wheat gluten is being extensively researched for use in the production of long-lasting bioplastics. Despite its brittle structure, the material's structure can be improved with additives and fillers. Wheat gluten's high protein content makes it promising for a variety of applications [19]. Sisti (2016) defines PBS as one of the newest biopolymers that could meet increased bioplastic demand in the market. PBS is usually preferred over low-density polyethylene and polypropylene. Biodegradable materials can be made from either biomass or fossil fuels. PBS is a highly sought-after material in the textile industry due to its ease of processing. It is used in the production of melt blown, multifilament, monofilament, flat, and split yarn, as well as in the manufacture of molded plastic products. Combining Spirulina with PBS enables the economical production of bioplastics based on Spirulina [20].

MATERIALS IMPROVED THE BIOPOLYMER PRODUCTS

To improve the flexibility and processability of biopolymer products, plasticizers are commonly added. These are large organic molecules that can mix with the material, and their efficiency depends on their ability to soften the target material. Among the plasticizers used in bioplastic production using microalgae, glycerol ($C_3H_8O_3$) [19, 20, 23] is the most frequently employed one, as shown in Table 3. Glycerol improves the availability of macromolecules for degradation[10], enhances flexibility and extensibility, and leads to phase-rich products with improved elongation [23]. Ciapponi et al. (2019) conducted a study comparing the plasticizing abilities of glycerol, octanoic acid, and 1,4-butanediol with wheat gluten and microalgae as fillers. According to the results of various tests, glycerol and 1,4-butanediol are efficient in the plasticization process because of their water permeability[19]. In addition, carboxymethylcellulose was used to enhance the mechanical properties of the produced plastic [21]. This substance is produced as a by-product of the reaction between cellulose, alkali, and chloroacetic acid. It dissolves easily in cold water, has low viscosity, and is thermally stable.

Table 3. Plasticizers and compatibilizers

Plasticizers and Compatibilizers	Chemical Formula	Purpose of Usage	Reference
Glycerol	$C_3H_8O_3$	Plasticizer	[19,20,23]
Octanoic acid	$C_8H_{16}O_2$	Plasticizer	[19]
1,4-butanediol	$C_4H_{10}O_2$	Plasticizer	[19]
EG	$C_2H_6O_2$	Plasticizer	[11]
CMC		Plasticizer	[21]
MA	$C_4H_2O_3$	Compatibilizer and grafting PVA	[19,23]
PE-g-MA		Compatibilizer	[11]
KPS	$K_2S_2O_8$	Compatibilizer initiator	[23]
DMSO	$(CH_3)_2SO$	Compatibilizer initiator	[23]

TECHOLOGIES OF MICROALGAE- POLYMER BLENDS

Compression molding is the most common method for producing microalgae-polymer blends, in which a mixture of biomass, polymers, and additives is placed in a mold and compressed at elevated pressure and temperature for a short period of time to form bio-composites. In the current literature, the temperature, pressure, and time parameters vary significantly. The reported temperatures used range from 130 °C to 160 °C, compression pressures from 20 kPa to 10 MPa, and molding times from 3 to 20 minutes.

The mixtures must be uniformly mixed prior to the molding process. Some publications use heating and what is known as melt mixing during this step. The parameters used during this step, like those used in compression molding, are not standardized and are determined by the researchers. Fabra et al. (2018) used a Brabender internal mixer designed for material research to melt mix their blends for 4 minutes at 130 °C and 60 rpm before compression molding. Otsuki et al. (2004), on the other hand, used a simpler roller mixer for melt mixing at 160 °C for 7.5 minutes. They used the same process to create MA-modified PE prior to blend homogenization to aid in the binding of microalgae biomass to the polymer material [17]. Aside from compression molding, some studies adapted variations that did not include the pressure element. Dianursanti et al. (2018) formed their prototypes by heating the melt-mixed mixture in molds in ovens without compression [23]. Critically if evaluate the advantages and disadvantages of using microalgae as a source of biomass for polymer blends compared to traditional sources such as corn or soy. This could include factors such as scalability, cost, and environmental impact. Secondly proposed is to analyze the effectiveness of the different methods used to produce microalgae-polymer blends and to discuss the limitations of each method, as well as to propose potential improvements or alternatives. Thirdly, the author can assess the mechanical and physical properties of the resulting blends, such as strength, flexibility, and biodegradability. The author can analyze how these properties. Lastly, the author can critically evaluate the potential applications and commercial viability of microalgae-polymer blends in various industries, such as packaging, textiles, and construction. The author can consider factors such as market demand, regulatory hurdles, and competition from alternative material.

CONCLUSION AND RECOMMENDATIONS

The current study is focused on biopolymer production from microalgae materials. The most common and successful microalgae species used in the production of both biopolymers and plastic (petroleum in origin) blend, are Chlorella and Spirulina species. It has been found that the quality of the final product of biopolymers should be improved by using additive such as plasticizers and compatibilizers. The outcomes of the review also discovered that there is still a need for more development of bioplastics production processes from microalgae with different species which have more bioplastic content in their wall structure to overcome the economic feasibility problems in industrial-scale implementations, that prevents wider usage of bioplastic products from single specis microalgae in the market. The biorefinery concept where bioplastic is produced from by-products of high-value chemical production from microalgae is promising and should give more attention to researchers and manufacturers in producing good biopolimer product with microalgae. Moreover, the use of various additives may restrict the implementation areas of the microalgae products, such as in food packaging and health care as well as their negative environmental impact. Therefore, further research is necessary to optimize the process for industrial applications and decrease additive usage by more innovative design.

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