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Microalgae as a Source of Biopolymer - A Comprehensive Review

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Abstract

The growth in overall demand for plastic materials has given rise to the manufacture and utilization of plastic articles throughout the world. This has led to extreme waste production, negatively influencing terrestrial and marine life. Microplastics lead to the endangerment of health. Therefore, plastic decomposition is a difficult task. Chemical treatments, recycling, carbonizing, and landfills aren't ideal solutions for lowering plastic pollution. As a result of this, there is a need to research and identify alternatives that decompose much more rapidly like biodegradable plastics when compared to synthetic plastics. Biodegradable plastic can be produced by algae which contain polysaccharides. Microalgae process a huge amount of lipids, proteins, and carbohydrates which are significant substances in the formation of biopolymers. Owing to their high growth rate and volume, they can be cultivated in wastewater. This review examines the capability of microalgae to produce biodegradable plastic and its economic possibility. Each of the latest sustainable methods has been considered in this article: plastic biodegradation and bioplastic production using microalgae.

Keywords: Biodegradable bioplastic, Non-biodegradable bioplastics, Bioplastic sources, Polyhydroxyalkanoates (PHA) Microalgae

Introduction

Currently, the annual bioplastic production around the world is 1%. In the past few years, the production of plastic-based materials has increased by over 368 million metric tons (Rajpoot *et al.*, 2022). Every year, approximately 8 million tons of plastic waste aredumped into oceans, jeopardizing the current waste management infrastructure (AlHussain *et al.*, 2022; Cywar *et al.*, 2022). Due to their insolubility, synthetic plastics lead to waste collection in landfills thereby threatening the environment. Therefore, numerous analyses have been carried out to enable the production of biodegradable plastic from green, brown, and red algae because of their rapid decomposition potential (Thiruchelvi *et al.*, 2021; Dhanasekar *et al.*, 2022). Microalgae contain renewable biomass such as starch, protein, cellulose, hemicellulose, and lignin which may be used to induce quality bioplastic (Do Val Siqueira *et al.*, 2021; Alhazmi *et al.*, 2022). Biodegradable plastic can help in reducing pollution due to its rapid decomposition thereby reducing expenditure on eliminating mishandled plastic waste (Halimah et *al.*, 2022; Ranganadhareddy, 2022). Possessing myriad characteristics, bioplastic materials can be categorized based on two factors: biodegradable or non-biodegradable/bio-based or fossil-based.

Biodegradable Plastic

Plastics are bio-based, biodegradable, and are obtained from renewable natural resources which indicate the property of biodegradation. Examples include thermoplastic starch, polyhydroxyalkanoate (PHA), polylacticacid (PLA), and Polybutylene succinate (PBS) (Jaffur *et al.*, 2021). Usually, PHAs are made from bacteria that primarily consist of sugar or lipids as the intracellular product. About 250 different microorganisms are employed in the production of PHA (Mosca *et al.*, 2020; Wei *et al.*, 2020). In this process, bioplastics occur during the destruction of bacteria, specifically when separated from the microcells. Likewise, polyhydroxyalkanoate (PHAs) consist of a fine shielding property helpful in providing a satisfactory variety of biological applications as shown in **Figure 1**. PHAs are biodegradable in water and soil (Sid *et al.*, 2021). They also have printability to oil and grease up to 120ºC as well as high resistance (Nazareth *et al.*, 2019). In polyhydroxyalkanoates, biodegradability is associated with the structure of the polymer as shown in Polycaprolactone (PCL) with a low melting point (60ºC) is biodegradable polyester. It is used in a wide variety of biological applications such as surgical structures (Chen & Zhang, 2018).

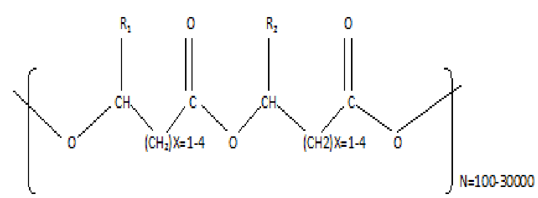

Figure 1. Structure of Polyhydroxyalkanoates with R_1 and R_2 are alkyl groups (C-C) (Ranganadhareddy, 2022)

Non-Biodegradable Plastic

Some bioplastics are non-biodegradable and hence pose a waste management issue (Meenakshi *et al.,* 2022). Examples of bio-based or partially bio-based non-biodegradable plastics include Bio-poly-ethylene (Bio-PE), Bio-poly-propylene (Bio-PP), Poly-trimethylene-terephthalate (PTT), and Poly-ethylene-terephthalate (PET). Manufactured from renewable natural resources like biomass and bioethanol, they may lack biodegradability (Ranganadha *et al.*, 2020; Van Roijen & Miller, 2022). These reckon for 40% of bioplastic manufacturing

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capacity in the world or around 0.8 million tons. Poly-ethylene-furoate (PEF), which is similar to poly-ethylene-terephthalate (PET), is bio-based and also consists of good shielding qualities, rendering it perfect for the making of bottles for beverages (Haas *et al.*, 2022).

Pathway for the Synthesis of Polyhydroxyalkanoates

PHB, the most common homopolymer among PHAs, has been widely studied concerning a variety of bacteria. The use of glucose for the production of PHA is the most prevalent pathway in bacteria. This process leads to the production of acetyl-CoA and NADPH via glycolysis and the pentose phosphate pathway. Further, the enzyme, β-ketothiolase (PhaA) is used to convert acetyl-CoA into acetoacetyl-CoA. In the following step, the NADPH serves as a cofactor for the acetoacetyl-CoA dehydrogenase enzyme (PhaB) to reduce it to 3-hydroxybutyryl-CoA. P (3HB) polymerase (PhaC) catalyzes the final step in the synthesis of PHB, which occurs when the 3-hydroxybutyryl-CoA polymerizes into PHB (Mohapatra *et al*., 2017). In addition, increasing the ratio of NADPH to NADP+ boosts the production of PHA (Alsiyabi *et al*., 2021). Three main pathways for microbial PHA synthesis have been revealed through studies involving the biosynthesis of PHA. Three enzymes, PHA synthase, β-ketothiolase, and NADPH dependent acetoacetyl-CoAreductase are mainly involved in the governing of Pathway I of the biosynthesis of PHA. *phaC*, *phaA*, and *phaB*, respectively, encode theseenzymes (Syahirah *et al*., 2020; Natarajan *et al*., 2022). It was reported that *Ralstonia eutropha* follows this pathway for the PHA synthesis. Microorganisms utilize fatty acids as part of Pathway II of PHA synthesis (Costa *et al*., 2018). PHA monomers are synthesized from acyl-CoA produced following fatty acid β-oxidation. Enzymes involved in this pathway include epimerase, 3-ketoacyl-CoA, acyl-CoA oxidase (putative), and (*R*)-enoyl-CoA hydratase/enoyl-CoA hydrataseI. The 3-hydroxyacyl-CoAmoleculefunctionsas a precursor molecule for the synthesis of PHA. Numerous microorganisms such as *P. aeruginosa*, *Aeromonas hydrophila*, and *Pseudomonas putida* synthesize MCL-PHAs. Two key enzymes, malonyl-CoA-ACP transacylase (FabD) and 3-hydroxyacyl-ACP-CoA transferase (PhaG) are required for the pathway III for the synthesis of PHA. 3-hydroxyacyl-ACP, from which 3-hydroxyacyl-CoA is then formed, is the precursor supplied by these enzymes. PHA synthase then catalyzes the process of synthesizing PHA **Figure 2** (Zhang *et al*., 2020; Remizova *et al*., 2022; Taher *et al*., 2022).

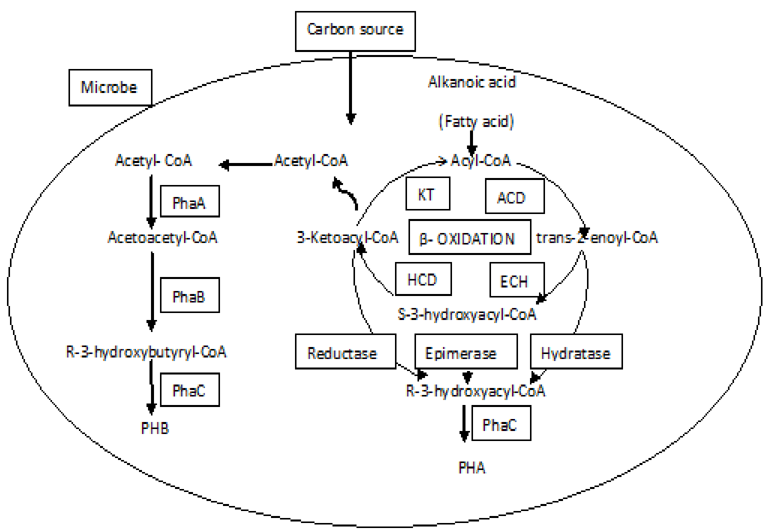

Figure 2. Biosynthetic pathway of Polyhydroxtbutyratye in microbes (Ranganadha *et al*., 2021)

Bioplastic Sources

Agricultural Crops

Bioplastics are made from proteins, polysaccharides, and other carbon sources (Haas *et al.,* 2022). Thermoplastic starch is the most extensively utilized bioplastic is thermoplastic starch, prepared either by modifying starch using hydrophilic plasticizers or by microbial fermentation and enzymatic saccharification. Nonetheless, plasticizers use starch-based bioplastics which are retained for long period and further recrystallize and cause mechanical characteristics to inhibit degradation. To solve this, nanocomposites created from starch-based bioplastics can be added to nanoparticles for usage in components of automobiles, materials utilized in packaging, and pharmaceutical delivery (Mukherjee *et al.*, 2019). By using a variety of terrestrial crops, starch is derived frequently. For the formation of bioplastic sheets, cassava starch was altered with glycerol, distilled water, and vinegar. Coconut husk fibers are also used to support cassava starch obtained bioplastics (Ozdamar & Murat, 2018). Tapioca starch will make excellent, elastic, and tough bioplastic, whereas starch derived from potato has traits of affluence and drying capacity. Bioplastics can also be made from proteins like wheat gluten. Due to bacterial sugar absorption, sugarcane can also be used to make bioplastics (Ranganadha *et al.*, 2020). Likewise, oil can be used for bioplastic synthesis as it is a useful carbon source.

Wastewater Sources

Wastewater, which consists of high salts and organic content, acts as a beneficial reserve that may be used for a diversity of schemes and aspirations (Zhou *et al.,* 2019). From two-stage processing comprising anaerobic fermentation and aerobic conversion using municipal wastewater, polyhydroxyalkanoates are formed. Also by wastewater treatment, PHBs may be produced by thermal cracking. Starch-based bioplastic is formed from the potato processing sector of wastewater (Hatti-Kaul *et al.,* 2020). Wood mill effluents and municipal sewage sludge are both wastewaters that have been scrutinized for bioplastic manufacture.

Organic Waste Sources

Food processing waste is an important advantage of bioplastics. Vegetable wastes are used to produce creative bioplastic films and agriculture wastes for starch or cellulose-based bioplastics (Jha & Kumar, 2019). Bioplastics can be formed with the help of various sources like rice bran, Kraft lignin extraction, and also microcrystalline cellulose extracted from the seeds of avocado, jackfruit, and peels of cassava (Othman *et al.,* 2021). There are two available choices for biodegradable plastic film manufacturing, namely cocoa pod husk and sugarcane bagasse (Ranganadhareddy, 2022).

Algae-Based Sources

Microalgae can be used as biomass for the manufacture of bioplastics and their cells are used for the extraction of starch and PHBs as shown in **Figure 3** (Ranganadha *et al*., 2021). Chlorella and spirulina play a major role in microalgae. Under the observation of an SEM microscope, they exhibit tiny cells, less than 50mm overall (Zhang *et al.,* 2019). The tiny cells enhance matrix dispersion, blending with poly olefins, making this microalgal biomass optimal for fiber and film applications where minute particle size is a major necessity. Therefore, spirulina and chlorella show greater delta and modulus values than those containing 80%-100% polyethylene samples. At 50%-65% polyethylene, spirulina has superior qualities tochlorella owing to its hydrophobic, nonpolar amino acids and sustaining interaction with polyethylene and chlorella. Chlorella performs great in 20%, 35%, and 80% concentrations of polyethylene as small percentages can blend easily in a separate phase. So chlorella has stronger bioplastic properties and spirulina is good at blends (Di Caprio *et al.,* 2020). Spirulina platens can also be used to fashion another highly biodegradable bioplastic. *Nannochloropsis* and *Phaeodactylum tricornutum* are additional microalgae or cyanobacteria used in the production of bioplastics (Abdo & Ali, 2019).

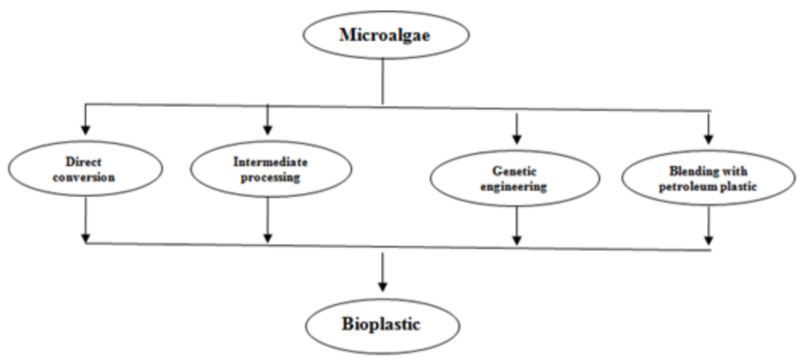

Figure 3. Algae conversion to bioplastic (Rajpoot *et al.*, 2022)

Polyhydroxyalkanoates

Microorganisms generated by polyhydroxyalkanoates are environmentally friendly and consist of properties corresponding to petrochemical polymers (Ranganadha & Chandrasekhar, 2021). Biopolymers are formed as a result of nitrogen deficit. Including PHA biopolymers, *Synechococcus subsalsus* and spirulina produce approximately 14-18 carbon chains. However, *chlorella minutissima* is unable to produce PHA biopolymers due to a lack of nitrogen. Microbial and culture strains changed the monomer makeup (Reddy *et al.,* 2017). These are linear polyesters made from sugar or lipid fermentation by bacteria. A mixed-integer nonlinear programming approach had been created to improve PHA plant conformation. This approach raises the plant's net values and aids in discovering suitable growing conditions (Kartik *et al.,* 2021). It also provides alternatives for biopolymer extraction from cells and also a method for unsheathing the number of biopolymers.

Production of Biopolymers from Algae Biomass

Algal biomass can be converted into biopolymers using three methods. Natural biopolymers are produced by cell factories within microalgal biomass (1st route), biopolymeric products are produced by fermenting microalgal biomass with microorganisms (2nd route), and composite microalgal biopolymers are produced by mixing microalgal biomass with some additives (3rd route) (Khan *et al.,* 2022). Using a source of light during photosynthesis, to create polymers inside the algal biomass is the first route. Microalgae require only a little amount of nutrition, rendering them ideal for biopolymer production. Changes in light intensity and frequency can induce the buildup of specific chemical compounds (Costa *et al.,* 2019). Adjusting the exposure time and intensity could result in more biopolymer production. However, UV irradiation can be utilized to synthesize biopolymers in an effortless and environmentally friendly method and gamma irradiation has been demonstrated to improve material qualities in recent years. Free radicals, produced by UV radiation, react with starch to generate cross-linked chains.

Therefore, UV could be employed to produce and construct biopolymers with appropriate properties. The fermentation process is included in the second path. During the fermentation process, algae-producing enzymes convert bio-mass into bio-products comprising biopolymers (Ananthi *et al.*, 2021; Aleidi *et al.*, 2022). Before the fermentation process, recent research concentrated on the extraction of important proteins, carbohydrates, and lipids and the fragmentation of algal biomass. A study presented a novel subcritical hydrothermal process for breaking down algal biomass with water and subsequently, fermented to form polyhydroxyalkanoates. The third approach is used to create algae-polymer mixtures. Compression is the most common method for creating bio-composites, which entails compressing of retaining microalgae and additives in a mold (Kardile & Shirsat, 2020; Choi *et al.*, 2022). Another frequently used process is solvent casting. In this, microalgae and additives are dissolved in a solvent and dried on surfaces to make films. PVA-algae is produced through this approach.

Applications

Food Packaging

The food industry is particularly concerned about pitfalls in packaging these days and is also always overseeing the requirements and grades of food processing around the world. The food industry's essential requirements of long-term sustainability and quality depend on the development of novel bioplastic-based packaging. Bioplastics that are easily compostable or degradable have the potential to fulfill the need for high-quality storage and also low-cost packaging with minimal impact on the environment, ease of actualization, and low restraint (Mostafavi & Zaeim, 2020). Oxygen permeability, moisture, and mechanical qualities are all important characteristics offood packaging. Two of the most prevalent needs for food packaging are water and oxygen protection.

Biomedical Applications

Polymers can be used for a wide range of medical and biological applications (Lippi & Plebani, 2020; Juliana *et al.*, 2021). In the biomedical field, advances in biodegradable polymers have led to the fruition of drug delivery systems and devices for tissue engineering. The diameter of the perforations in these membranes ranges from 60 to 300 mm. Nanocelluloses and their composites are heavily used in the research of bioplastics for the manufacturing of medical implants (Rol *et al.*, 2019).

3D Printing

In contemporary studies, 3D printing and magnetically sensitive nanocellulose-based materials have been produced. Because of their biocompatibility, polyhydroxyalkanoates are also suitable for application in the medical fields such as in the detection of cancer, post-surgical ulcer therapy, bone tissue engineering, wound healing dressings, artificial blood arteries, heart valves, and so on (Reddy *et al.*, 2019; Chen *et al.*, 2022; Chidambaranathan & Culathur, 2022).

Conclusion

Bioplastics derived from microalgal biomass can help address plastic concerns, expand the market for bioplastics, and contributeto environmental sustainability. This study looked into the current condition of the synthesis of bioplastics from microalgae resources. The sources, analyses, manufacture, implementation, and sustainability of bioplastics had been examined to define the field. Production of bioplastics without any need for chemical extraction is the optimal approach. However, the majority of microalgae biomass needs chemical treatment to transform it into bioplastic, leaving chemical waste behind. Nevertheless, green technologies can be used to make these bioplastics, but further improvement is necessary to optimize the downstream process of manufacturing microalgae bioplastics namely processing time, quality, cost and applications. Furthermore, to increase the mechanical properties of microalgal biomass, several additional biomaterials can also be employed as additives. The most common algae species used in the manufacture of bioplastics and plastic blends are chlorella and spirulina. To solve the economic viability concerns inhibiting the widespread usage of microalgae-based bioplastics up for sale, further research into microalgae-based bioplastic manufacturing processes is required.

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