Biotechnology Advances 60 (2022) 107999

Contents lists available at ScienceDirect

Biotechnology Advances

journal homepage: www.elsevier.com/locate/biotechadv

Research review paper

Biopolymers production from microalgae and cyanobacteria cultivated in wastewater: Recent advances

Savvas Giannis Mastropetros [a], Konstantinos Pispas [a], Dimitris Zagklis [a], Sameh S. Ali [b,c], Michael Kornaros [a,*]

[a] Laboratory of Biochemical Engineering & Environmental Technology (LBEET), Department of Chemical Engineering, University of Patras, 1 Karatheodori Str., University Campus, 26504 Patras, Greece
[b] Biofuels Institute, School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China
[c] Botany Department, Faculty of Science, Tanta University, Tanta 31527, Egypt

ARTICLE INFO

Keywords:
Biotechnology
Photosynthetic microorganisms
Bioplastics
PHA
PHB
Biodegradability
Biomass
Effluent management
Sustainability

ABSTRACT

Plastic materials are used to manufacture a broad variety of items with a short useful lifespan, resulting in significant amounts of waste material generation. This form of waste is often observed floating at sea, and different microplastics have been discovered in fish stomachs and women's placentas. Bioplastics are a more biodegradable substitute for fossil-based polymers. Microalgae are capable of producing poly (hydroxy alkanoate) esters (PHAs), aliphatic polyesters that are biodegradable. The most prevalent and well-characterized biopolymer is the poly (3-hydroxy butyrate) ester (PHB), which belongs to the short-chain PHAs. Under aerobic conditions, PHB compounds degrade fully to carbon dioxide and water. They are ecologically neutral, having thermal and mechanical qualities comparable to those of petrochemical polymers. Numerous microalgae species have been reported in the literature to be capable of making bioplastics under certain conditions (N-P restriction, light exposure, etc.), which may be exploited as a source of energy and carbon. To further ameliorate the environmental impact of microalgae culture for bioplastics production, a limited number of published studies have examined the accumulation of bioplastics, from microalgae grown in wastewater, at a concentration of 5.5–65% of dry biomass weight.

1. Introduction

Since the early 1950s, demand for and production of plastics have grown exponentially. Plastics provide conveniences, based on their physical and mechanical properties, by substituting materials such as glass, paper, metal, and wood in a variety of uses, primarily packaging and building (Lebreton and Andrady, 2019; Możejko-Ciesielska and Kiewisz, 2016). Conventional plastics are composed of petrochemical polymers (Das et al., 2018) and qualitatively distinguished by their great strength, durability, low density and cost (Van Eygen et al., 2017). Polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyamides (nylons) are all examples of plastic materials that are used to manufacture a wide variety of products, including automotive components, medical equipment, agricultural tools, and electrical and electronic devices (Leal Filho et al., 2019). In 2018, over 359 million tons of plastic were manufactured, 17% of which were generated in Europe (Plastics Europe, 2019), while industrial production of polymers is the second-largest usage of crude oil, behind energy production. (Martins et al., 2014).

Plastics consist of long chain, high molecular weight polymers with hydrophobic properties and are difficult to decompose under ambient conditions as they exhibit significant resistance against microbial degradation (Abdo and Ali, 2019; Lee and Liew, 2020). The resilience of plastics, combined with their limited usable life, has resulted in a

Abbreviations: ATPE, Aqueous Two-Phase Extraction; Tg, Glass Transition Temperature; GHG, Greenhouse Gas; LCA, Life Cycle Assessment; lcl-PHAs, Long-chain PHAs; mcl-PHAs, Medium-chain PHAs; Tm, Melting Temperature; PBAT, Polybutylene Adipate Terephthalate; PCL, Polycaprolactone; PBRs, Photobioreactors; PAR, Photosynthetically Active Radiation; PHB, Poly (3-hydroxy butyrate) ester; PHAs, Poly (hydroxy alkanoate) esters; PBS, Poly Butylene Succinate; PD, Poly Diallyldimethylammonium chloride; PVAC, Poly Vinyl Acetate; PVA, Poly Vinyl Alcohol; PE, Polyethylene; PET, Polyethylene Terephthalate; PLA, Polylactic Acid; PP, Polypropylene; PPC, Polypropylene Carbonate; PS, Polystyrene; PVC, Polyvinyl Chloride; scl-PHAs, Short-chain PHAs; SDS, Sodium Dodecyl Sulfate.

* Corresponding author.
E-mail address: kornaros@chemeng.upatras.gr (M. Kornaros).

https://doi.org/10.1016/j.biotechadv.2022.107999
Received 8 March 2022; Received in revised form 26 May 2022; Accepted 31 May 2022
Available online 3 June 2022
0734-9750/© 2022 Elsevier Inc. All rights reserved.

massive waste stream (Lee and Liew, 2020). Around 40% of plastics have a usage life of <1 month (Achilias et al., 2007), with plastic waste released into the environment being detrimental to marine, freshwater, and terrestrial ecosystems (Leal Filho et al., 2019). Both recycling and incineration are prominent solutions for managing plastic waste; while, recycling has been shown to be an unsustainable process due to the enormous amount of energy required (Das et al., 2018). Additionally, combustion of non-recyclable plastics is undesirable because it releases harmful substances into the environment, such as furans and dioxins (Lee and Liew, 2020). Plastic wastes have been classified as dangerous by recent studies (Rochman et al., 2013), with around 1 million animals dying each year as a result of petrochemical pollution (Cassuriaga et al., 2018). Plastic waste disperses across the oceans of the world, resulting in tiny plastic particles referred to as macro- and microplastics. Microplastics range in size from a few micrometers to 500 μm and are rarely visible to the human eye (Andrady, 2011; Eriksen et al., 2014). In 2014, 5.25 trillion plastic particles weighing 268,940 t were estimated to have drifted at sea (Eriksen et al., 2014). Due to the enormous surface area of microplastics, they are capable of adsorbing and accumulating hazardous compounds such as heavy metals and organic contaminants (Cox et al., 2019; Fang et al., 2019). Additionally, microplastics have the potential to penetrate the food chain and end up in human tissues (Browne, 2013; Cox et al., 2019). Numerous microplastics have been discovered in the stomachs of three distinct fish species in the Mediterranean Sea (swordfish, red and long-winged tuna), as well as in women's placentas (Ragusa et al., 2021). Recently, a team of researchers provided data on the discovery of various plastics' particles (such as PET, PS, PE) in human blood. More specifically, plastic particles derived from blood samples were identified and quantified using pyrolysis - gas chromatography / mass spectrometry. The concentration of total plastic compounds in the blood samples was found to be 1.6 μg ml^{-1} (Leslie et al., 2022). Clearly, plastic waste endangers not just marine life but also public health.

The buildup of plastic residues in the environment, the inability to handle such pollutants, the depletion of oil sources, and the resulting rise in greenhouse gas (GHG) emissions have generated an urgent need for sustainable ecological materials (Cassuriaga et al., 2018). Bioplastics, as defined by the European Union, are materials derived from biomass or biodegradable materials. Thus, plastics may be classified into four broad categories (European Bioplastics, 2017), (Fig. 1). The first category includes conventional petrochemical-derived plastics that are biodegradable under certain conditions, whilst the second one consists of common polymers that are not biodegradable, such as PP, PET, PVC and others. The third group includes biodegradable polymers derived from biological sources. The most typical products in this category are a few polyesters, such as polylactic acid (PLA) that is made from lactic acid, and PHAs, which are produced by a vast variety of microorganisms (Rahman and Bhoi, 2021; Razza and Innocenti, 2012). Finally, the fourth category encompasses bioplastics thar are not biodegradable materials (e.g., organic PE, organic PET).

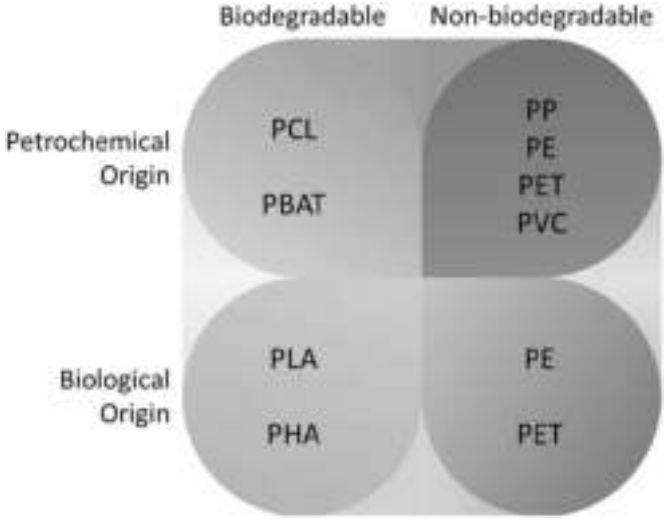

Fig. 1. Classification of plastics according to the EU (European Bioplastics, 2017).

Environmentally speaking, biodegradable polymers of biological origin provide a feasible solution to the plastic waste issue. Bioplastics are made from renewable materials and decompose either anaerobically or aerobically (Razza and Innocenti, 2012). However, combining bioplastics with conventional petrochemical-derived plastics to improve their properties (such as heat resistance, flexibility, and durability) may result in their non-biodegradable components accumulating as microplastics in the environment, contributing to the problem of plastic waste accumulation (Iwata, 2015).

Numerous life cycle assessment (LCA) studies have shown that substituting bioplastics for conventional plastics might result in a reduction in greenhouse gas emissions. In the past, using agricultural products to make bioplastics competed with the food industry as it required vast amounts of mineral resources for crop growth, since the bulk of bioplastics was created by fermentation of agricultural products such as maize, wheat, potatoes, rice, and soy (Abdo and Ali, 2019; Gironi and Piemonte, 2011, 2010). According to a recent approach, PLA is formed through the fermentation of rich-in-sugars substrates, such as lignocellulosic biomass and waste streams full of lignin and cellulose (Rahman and Bhoi, 2021).

In comparison, one promising alternate method for producing bioplastics involves the use of microalgae (Martins et al., 2017). Microalgae and cyanobacteria, as primary producers mainly of aquatic ecosystems, bind carbon dioxide, regulating its concentration in the atmosphere. In recent decades, these photosynthetic microorganisms have become known for their potential utilization in the field of energy production (Mat Aron et al., 2020). Unlike exclusively heterotrophic microorganisms, the research interest focuses on the fact that such microorganisms can grow following different metabolic pathways in lean and non-lean substrates (seawater, freshwater, effluents, and wastewater) and accumulate a variety of valuable components. Some of the most common high added value products derived from microalgal biomass are pigments, proteins, and lipids, while many species have been reported to accumulate intracellular polyesters for energy storage purposes. However, many obstacles remain to be surpassed in terms of productivity and cost of the overall process. The relatively low rates of biomass growth and accumulation of intracellular bioplastics could be overcome through a biorefinery strategy (Porras et al., 2017). Additionally, microalgae could exploit wastewater as a source of nutrients (e.g., anaerobic effluents from digested wastewater), lowering environmental footprint and production costs.

The aim of this review is to gather knowledge about the participation of photosynthetic microorganisms in the production of bioplastics. In this context, data on cultivation conditions, the quality of the substrates used and the productivity of bioplastics from already studied species are presented. Finally, part of the present study is devoted to the extraction methods of biopolymers and how they affect the properties of the bioplastic material.

2. Results and discussion

2.1. The role of polyesters in the biopolymers' group

2.1.1. The origin of poly (hydroxy alkanoate) esters (PHAs)

The PHAs are biodegradable aliphatic polyesters made of hydroxyalkanoic monomers that may be generated by a variety of bacteria and microalgae (cyanobacteria and eukaryotes) (Khanna and Srivastava, 2005; Martins et al., 2017). Maurice Lemoigne, a French scientist, discovered PHAs in 1920 when he noticed the Gram-positive bacteria

Bacillus megaterium forming intracellular granules mostly composed of PHB (Keshavarz and Roy, 2010). The synthesis of PHAs by microalgae and bacteria is often seen under physiological cell stress situations, such as a deficiency of phosphates and nitrogenous nutrients and a restriction on light supply regarding photosynthetic microorganisms (Cassuriaga et al., 2018; Możejko-Ciesielska and Kiewisz, 2016). PHAs are intracellularly synthesized as an alternative energy source for the cell (Kavitha et al., 2021; Mahishi et al., 2003; Możejko-Ciesielska and Kiewisz, 2016; Singh et al., 2017; Vanessa et al., 2015). When external carbon supply is depleted, intracellular macromolecules depolymerize to offer a source of carbon and energy (Możejko-Ciesielska and Kiewisz, 2016). There have been 155 PHA monomers discovered so far, with molecular weights ranging from 50×10^3 to 1×10^6 Da. Monomeric PHAs are classified into three classes based on their carbon atom count: short-chain PHAs (scl-PHAs) contain between three and five carbon atoms, medium-chain PHAs (mcl-PHAs) contain between 6 and 14 carbon atoms, and long-chain PHAs (lcl-PHAs) contain between 15 and 20 carbon atoms (Singh et al., 2017). PHAs exhibit high crystallinity, from 60% to 80%, and melting temperature (T_m) between 50 °C and 180 °C (Keshavarz and Roy, 2010; Khanna and Srivastava, 2005; Rahman and Miller, 2017; Singh et al., 2017).

The most abundant and well-studied biopolymer in the PHA category is PHB, which belongs to the short-chain PHAs. Biocompatibility, biodegradability, hydrophobicity, non-toxicity, and piezoelectric capability are all characteristics of PHB. Additionally, it has a melting point of approximately 180 °C and a tensile strength of 40 MPa. These qualities make it a viable alternative to traditional petrochemical plastics (Abdo and Ali, 2019; Ansari and Fatma, 2016; Haase et al., 2012; Rahman and Miller, 2017; Singh et al., 2017). There is growing evidence that PHB monomers are also non-toxic (Chen and Wu, 2005). Under aerobic conditions, PHB compounds degrade fully to carbon dioxide and water, but are converted to methane during anaerobic decomposition (Cassuriaga et al., 2018). To summarize, the above-mentioned facts pave the way for a broad variety of PHA-based applications, ranging from materials packaging to industrial, agricultural, and medicinal uses (Keshavarz and Roy, 2010).

2.1.2. Biodegradation of PHAs in different natural environments

Biodegradation is a term that refers to a collection of biological processes that breakdown and convert organic matter to inorganic matter. Biodegradation is carried out by degraders, which are microorganisms (fungi, bacteria, and protozoa) that proliferate on decomposing organic matter, which is formed by ecosystems. This is a critical environmental mechanism that minimizes pollution caused by organic wastes (Razza and Innocenti, 2012).

Because polymers are made up of lengthy and heavy chains, they cannot pass through the cell membrane into the cell, which is where cellular metabolism occurs. The biodegradability of polyesters derived from biological sources (PHAs, PLA) is supported by the presence of specialized enzymes known as esterases. To be more precise, the biodegradation of PHAs in the environment starts with hydrolysis and oxidation processes catalyzed by the extracellular enzymes released by degraders (Razza and Innocenti, 2012). This method results in the formation of oligomers, dimers, and low molecular weight monomers from the polymer chains (Roohi et al., 2018). These microbes utilize the carbon contained in polymer chains to generate energy, CO_2 or other biomolecules required for growth. Aerobic or anaerobic microbial biodegradation is possible. Aerobic biodegradation occurs when heterogeneous organic materials are decomposed into carbon dioxide and water by a mixed microbial population, resulting in the simultaneous generation of large quantities of biomass (Fig. 2). Aerobic conditions and a humid and warm environment are required for this process to take place. In the case of anaerobic biodegradation, the breakdown of organic matter eventually leads to the synthesis of methane, carbon dioxide, and water in the absence of oxygen, resulting in lower biomass production (Fig. 2) (Costa et al., 2018b; Razza and Innocenti, 2012; Roohi et al., 2018).

2.2. Bioplastics production from single cell photosynthetic life forms

Plastic contamination at seas and around coasts is increasing even in areas with little human activity. Therefore, the development of models for monitoring and predicting levels of plastic pollution was a necessity and remains a major research topic (Galgani et al., 2021). Bioplastics have been a significant area of study in terms of commercialization. PHAs are ecologically friendly, with thermal and mechanical qualities comparable to those of traditional petrochemical polymers. Bacteria have been shown to be the most effective microorganisms in the manufacturing of polyhydroxyalkanoates, with a productivity of up to 3.2 g L^{-1} h^{-1} (Singh et al., 2017). However, heterotrophic biomass

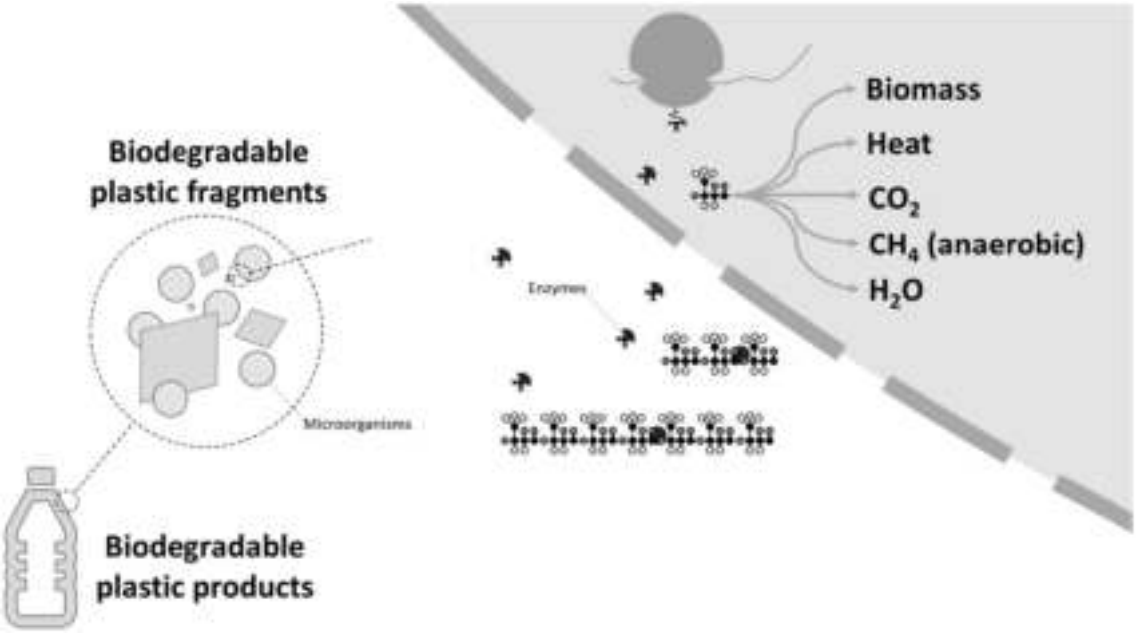

Fig. 2. Aerobic and anaerobic degradation of PHB.

demands a significant capital investment due to the high cost of carbon sources, the high oxygen demand, and the energy-intensive product recovery methods. In comparison, microalgae and cyanobacteria are a more ecological and cost-effective way to synthesize PHAs. Microalgae present an advantageous solution because of their low nutritional requirements and their ability to photosynthesize by capturing carbon dioxide and using solar energy. Additionally, such microorganisms may grow on a variety of substrates, including wastewater, and demonstrate rapid growth rates. Wastewater treatment combined with the generation of PHAs may be a viable future environmental strategy for reducing carbon dioxide emissions and thereby mitigating the greenhouse effect (Samantaray and Mallick, 2015; Singh et al., 2017).

2.2.1. Main characteristics of microalgae & cyanobacteria

Algae are a diverse group of multicellular and unicellular organisms capable of carrying out photosynthesis, producing oxygen at the same time. There is a classification into two broad groups according to their size. The macroalgae group includes cells ranging from a few centimeters to several meters, while microalgae are organisms with size up to a few hundreds of micrometers. Microalgae are eukaryotic photosynthetic microorganisms, in contrast to cyanobacteria, which are purely prokaryotic cells; nonetheless, this difference is sometimes blurred in the published literature, with cyanobacteria being included alongside microalgae. Both eukaryotic microalgae and procaryotic cyanobacteria are major primary producers in aquatic habitats (Markou and Nerantzis, 2013). The oceans, which cover around 71% of the planet's surface, are home to over 5000 species of microalgae, which form the foundation of the marine food chain and account for 70% of the world's biomass production and 50% of the atmospheric oxygen (Barsanti and Gualtieri, 2014).

Both microalgae and cyanobacteria are phototrophic organisms that may use a variety of alternate metabolic pathways in response to changing environmental circumstances (Rizwan et al., 2018; Singh et al., 2017). Three distinct mechanisms of metabolism are recognized. To grow autotrophically, cells use carbon dioxide or another form of inorganic carbon and absorb light to meet their energy requirements. Organic substances (acetic acid, maltose, glucose, etc.) are digested in the heterotrophic metabolism as a source of carbon and energy. Microalgae may employ either sunlight or organic substances as a source of energy by combining autotrophic and heterotrophic growth, and carbon can be obtained in either inorganic or organic form (Rizwan et al., 2018; Singh et al., 2017). *Arthrospira platensis*, *Chlorella vulgaris* and *Haematococcus pluvialis* are examples of mixotrophic species (Rizwan et al., 2018).

Additionally, the plethora of biochemical and physiological features make microalgae a lucrative economic resource. Microalgae create a variety of biological compounds as a result of their metabolic processes, including pigments, proteins, lipids, carbohydrates, and biopolymers (Koutra et al., 2018a). Commercial applications of microalgal biomass include the food sector, organic fertilizer manufacturing, and the formulation of medicines and antimicrobial medications (Koutra et al., 2018a; Rizwan et al., 2018). As indicated earlier, microalgae are also used in environmental applications, such as carbon dioxide fixation, wastewater treatment, and bioremediation of heavy metals (arsenic (As), lead (Pb), and mercury (Hg)), among others (Kwon et al., 2017; Spain et al., 2021).

2.2.2. Growing conditions of microalgae

Microalgae growth requires an appropriate supply of inorganic carbon (CO_2, HCO_3^-) and light for photosynthesis to occur. As previously stated, carbon may also be given in the form of sugars, acids, and alcohols. Apart from carbon, nitrogen is the most critical nutrient for biomass formation. The nitrogen concentration of biomass may vary between 1% and 10%, or even more. Nitrogen is mostly digested by microalgae as nitrates (NO_3^-), however ammonium (NH_4^+) or urea may also be employed without impairing their growth rate. Additionally, phosphorus is required for growth and a variety of cellular processes, including energy transfer and nucleic acid synthesis. Microalgae prefer orthophosphates (PO_4^{3-}) as phosphorus source. Sulfur (S), potassium (K), sodium (Na), iron (Fe), magnesium (Mg), and calcium (Ca) are also critical, as are trace elements such as boron (B), copper (Cu), manganese (Mn), and zinc (Zn). Microalgae may use around 30 minerals and other chemical substances. In general, the biomass production of microalgae is variable and is influenced by a number of parameters, including the microalgae species, nutrients, light intensity, temperature, pH, substrate concentration, and culture purity (Richmond, 2004).

Microalgae may grow in either open or closed bioreactor systems. Cultures grow in natural or manufactured open outdoor ponds and puddles in open-type systems. Closed systems, referred to as photobioreactors (PBRs), are constructed from a variety of transparent materials, such as plastic or glass, and vary in terms of design and function. Photoreactors are classified as flat or tubular, horizontal, inclined, vertical, spiral, or helical, depending on their design (Richmond, 2004). Although open tanks are more durable, easier to construct, and less expensive to operate, the majority of microalgae cannot be stored in them for extended periods of time due to the high risk of contamination by fungi, bacteria, and protozoa, as well as competition with other microalgal strains that typically dominate the culture. In comparison, photobioreactors provide more protection against contamination and greater control over the conditions, assuring the chosen strains' dominance (Rizwan et al., 2018). The culture system chosen is determined by a number of elements, most notably the strain's nature, the availability of nutrients, the environment, the cultivation technique, and the desired end use of biomass. (Markou and Nerantzis, 2013; Rizwan et al., 2018).

2.2.3. PHB production by microalgae

Today, about 100 strains of eukaryotic and prokaryotic (cyanobacterial) microalgae have been identified as capable of photoautotrophically accumulating PHB at concentrations ranging from 0.04% to 80% of their dry mass (Cassuriaga et al., 2018; Kavitha et al., 2016). Following that, the majority of research concentrates on altering growth conditions in order to maximize and optimize PHB production by various microalgae strains. According to reports, the most significant factors that contribute to the accumulation of PHB in microalgae biomass are, the presence of organic carbon (such as acetic acid, pentoses, etc.) (Abdo and Ali, 2019; Zhang and Bryant, 2015), the light exposure time reduction (Costa et al., 2018b), the limitation of nitrogen and phosphorus (Krasaesueb et al., 2019; Martins et al., 2014; Samantaray and Mallick, 2015), the limitation of certain heavy metals (Ni and Cu) (Samantaray and Mallick, 2015), and the dissolved gas transfer resistance in the culture (Samantaray and Mallick, 2015).

Numerous strains may collect significant quantities of bioplastic PHB and its copolymers when cultivated under the conditions described above. This concentration may reach as high as 80% of their dry mass. Among the green microalgae, some cyanobacteria have been shown to accumulate PHB during mixotrophic growth, including *Nostoc muscorum*, *Spirulina platensis*, *Aulosira fertilissima*, and *Synechocystis* sp. The polymer content of these strains varied between 29% and 85% (on a dry biomass basis), depending on the species produced and the culture medium used (Ansari and Fatma, 2016). Table 1 summarizes microalgae that have been described in the literature to be capable of producing PHAs.

2.2.4. Properties and applications of PHAs

Among other biodegradable plastics (such as PLA or starch-based polymers), PHAs have gained prominence owing to their diverse chemical structures and distinctive material properties (Keshavarz and Roy, 2010). Environmentally speaking, since high-density PHA pieces do not float in aquatic habitats, they will be submerged and decomposed by surface biogeochemical processes once disposed (Balaji et al., 2013; Costa et al., 2019; Costa et al., 2018a). PHAs are fully biodegradable, and their biocompatibility makes them ideal for use in healthcare and

Table 1
Brief overview of species reported in literature as able to produce PHAs.

Species	Type of PHAs	PHA Content (%)	Cultivation conditions	Days	References
Spirulina LEB. 18	PHB	44.19	8.4 g L^{-1} sodium bicarbonate and 0.25 g L^{-1} sodium nitrate, 30 °C, 12 h photoperiod, 3200 lx	15	(Martins et al., 2014)
1) *Spirulina* sp. LEB 18 2) *Nostoc ellipsosporum*	PHB	1) 20.62 2) 19.27	30 °C, 12 h photoperiod, 41.6 μmol m-2 s-1	1) 15 2) 10	(Martins et al., 2017)
Chlorella pyrenoidosa	PHB	27.0	Fogg's medium (without agar), 80 lx	14	(Das et al., 2018)
Synechocystis sp. PCC 6714	PHB	16.4	nitrogen and phosphorous deficiency, 28 °C, 40 μmol m^{-2} s^{-1}, 20 mL min^{-1} 2% CO_2	14	(Kamravamanesh et al., 2017)
Synechococcus sp. MA19	PHB	55.0	phosphate deficiency, 50 °C, 50 W m^{-2}, 100 mL min^{-2} 2% CO_2	11	(Nishioka et al., 2001)
Synechocystis sp. PCC6803	P3HB	7.0	Sodium acetate supplementary, 30 °C, 150 μmol m^{-2} s^{-1}	8 days (1st stage) 8 days (2nd stage)	(Sudesh et al., 2002)
Synechococcus elongates	PHA	17.15	Nitrogen deficiency, 1% sucrose, 24 °C, light/dark (14/10 h)	15	(Mendhulkar and Shetye, 2017)
Synechococcus elongates	PHA	7.02	Phosphate deficiency, 1% fructose, 24 °C, light/dark (14/10 h)	15	(Mendhulkar and Shetye, 2017)
Nostoc muscorum	P(3HB-co-3 HV)	31.4	NO_3 free BG11, 0.11% acetate, pH 8.1, 25 °C, 75 μmol m^{-2} s^{-1}, light/dark (14/10 h)	16	(Mallick et al., 2007)
Nostoc muscorum	P(3HB-co-3 HV)	78	Nitrogen deficiency, pH 8, 25 °C, 75 μmol m^{-2} s^{-1}, light/dark (14/10 h)	7	(Bhati and Mallick, 2015)
Spirulina platensis	P(3HB)	10.0	Nitrogen deficiency, 0.5% Sodium acetate, pH 9, 25 °C, 1020 lx	10 days (1st stage) 15 days (2nd stage)	(Toh et al., 2008)
Synechocystis sp.	P(3HB)	14	Nitrogen deficiency, 0.5% Sodium acetate, pH 7.1, 25 °C, 1020 lx	10 days (1st stage) 15 days (2nd stage)	(Toh et al., 2008)
Synechocystis sp.	PHB	28.8	Pre grown in BG11 + 0.1% glucose, Phosphorous deficiency, 0.4% acetate, pH 8.5, 28 °C, 75 μmol m^{-2} s^{-1}, light/dark (14/10 h)	21 days (1st stage) 10 days (2nd stage)	(Panda et al., 2006)
Synechococcus subsalsus	PHA	16	nitrogen deficiency, 28 °C, 41.6 μmol m^{-2} s^{-1}, light/dark (12/12 h)	15	(Costa et al., 2018a)
Chlorogloeopsis fritschii PCC 9212	Poly-3-hydroxybutyrate (P3HB)	5.0	BG-11, 26 °C, 50 μmol m^{-2} s^{-1}, 1% (*v*/v) CO_2 acetate deficiency	18	(Zhang and Bryant, 2015)
Chlorogloeopsis fritschii PCC 9212	Poly-3-hydroxybutyrate (P3HB)	15.0	BG-11, 26 °C, 50 μmol m^{-2} s^{-1}, 1% (v/v) CO_2 10 mM acetate	18	(Zhang and Bryant, 2015)
Scytonema geitleri	PHB	7.12	Chu − 10, 30 °C, pH 8.5, 95 μmol m^{-2} s^{-1}, Light/dark (14/10 h), 30 mM acetate	28	(Singh et al., 2019)
Anabaena sp.	PHB	46	Jaworski medium, 27 °C, 90–120 μmol m^{-2} s^{-1}, 5 g L^{-1} Sodium Acetate, Phosphorous deficiency	7	(Simonazzi et al., 2021)

medicine (Costa et al., 2019). The extensive usage of PHAs in a variety of industries is due to their thermoplasticity, which is accompanied by hydrophobicity, insolubility in water, and resilience to oxidative environments (Balaji et al., 2013; Bugnicourt et al., 2014; Costa et al., 2019; Sharma et al., 2021). Additionally, these bioplastics exhibit optical purity while displaying a high resilience to ultraviolet irradiation (compared to polypropylene) (Bugnicourt et al., 2014; Markl et al., 2019).

PHB, the most prevalent subgroup of the PHAs group, has several properties similar to those of traditional plastics (such as PP, PE, and PS), which may make PHB an excellent substitute for petrochemical plastics (Domínguez-Díaz et al., 2015; Khanna and Srivastava, 2005). For example, PHB has a higher melting point in comparison with PP and PS and a comparatively high tensile strength (Khanna and Srivastava, 2005). Additionally, PHB homopolymer fibers have a hard-elastic behavior. The high degree of crystallinity, brittleness, and very low elongation at break, all place substantial constraints on the use of PHB in a broad variety of applications, including the manufacturing of durable building materials (Aydemir and Gardner, 2020; Bhati and Mallick, 2012; Muneer et al., 2020).

In general, crystallinity levels above 50% are deemed undesirable for industrial and commercial usage, since they raise fragility (Laycock et al., 2013). PHB's brittleness is directly connected to its near-room temperature glass transition temperature (Costa et al., 2019; Markl et al., 2019; Muneer et al., 2020), thus, storing PHB under ambient conditions is likely to result in increased brittleness and stiffness (Domínguez-Díaz et al., 2015). A common remedy for this material failure is the inclusion of plasticizers, which increase molecular mobility and decrease the glass transition point.

Additionally, the temperature at which the PHB undergoes thermal degradation is extremely near to its melting point, often resulting in processing failures (Aydemir and Gardner, 2020; Domínguez-Díaz et al., 2015). In contrast to the previously stated facts, mcl-PHAs and co-polymers seem to be more suited for commercial and industrial applications, owing to their lower degree of crystallinity and lower melting point. This kind of PHA is less brittle and stiff, due to its improved elasticity and significantly increased elongation at break (Rahman and Miller, 2017).

PHAs' physical qualities are determined by the molecular weight and quality of their monomers (Bugnicourt et al., 2014). It is critical to stress that the procedures employed to extract PHAs have a direct effect on the chemical makeup (monomeric sequences) and consequently on the polymer's physical properties. Variations in molecular weight are caused by different extraction and recovery procedures, resulting in a diversity of crystallinity levels and durability (Costa et al., 2018a). Additionally, the chemical makeup (monomeric composition) of PHAs is

determined by the biological synthesis method and microorganism that produces them. Finally, chemical modification (through chlorination, cross-linking, epoxidation, hydroxylation, and carboxylation) is recommended to modify the profile of biologically generated PHA and tailor its properties to the intended use (Koller et al., 2010). A comparison of the most commonly used fossil-derived plastics and microalgae produced plastics is presented in Table 2.

2.3. Wastewater substrates for microalgae cultivation

Due to the high water and nutrient needs, industrial microalgae biomass production is deemed unprofitable. On the contrary, using wastewater as a substrate for microalgae growth is a cost-effective and convenient choice. Microalgae and cyanobacteria consume organic carbon, inorganic components such as nitrogen, phosphorus, and micronutrients found in wastewaters (Bhati and Mallick, 2015; Koutra et al., 2021; Rahman et al., 2012). Additionally, microalgae are capable of bioremediating some hazardous heavy metals found in industrial waste, such as arsenic, beryllium, chromium, lead, and mercury (Das et al., 2018; Rahman et al., 2012). Following that, using wastewater as a substrate for microalgae growth is a potential, alternative, environmentally friendly, and economically viable approach for combining the production of high-added-value chemicals with wastewater management.

Early-stage research in the subject of microalgal culture in wastewater is being performed with the goal of producing bioplastics, especially PHAs (Fig. 3). Evidence shows that it is possible to generate large concentrations of PHAs with characteristics equivalent to those of commercial plastics. Indicatively, (Krasaesueb et al., 2019) isolated bioplastic PHB in the cyanobacterium *Synechocystis* sp. PCC 6803 (ΔSphU) which was cultured on shrimp farm waste under nitrate limiting conditions. Another study showed a copolymer P(3HB-co-3 HV) production in the cyanobacterium *N. muscorum Agardh* grown on 10% chicken waste with CO_2 enrichment and 0.28% acetic acid, 0.30% valeric acid, and 0.38% glucose (Bhati and Mallick, 2016).

Anaerobic digestion is a critical process in the domain of renewable energy generation and waste management. Organic matter is consumed by bacteria and archaea during anaerobic digestion, leading to the formation of biogas. Biogas is a kind of renewable energy source that is mostly composed of methane and carbon dioxide. As a result of this process, a considerable amount of wastewater known as digestate is produced (Bjornsson et al., 2013; Kaur et al., 2020; Koutra et al., 2018b). Digestates are considered as a rich source of inorganic nutrients (ammoniacal nitrogen and phosphorus) (Ayre et al., 2017; Bjornsson et al., 2013; Kaur et al., 2020). These features make digestates appropriate as microalgae culture substrates. Microalgae may also develop in digestates with very high concentrations of ammonium nitrogen (800–1600 mg N-NH_4^+ L^{-1}), which are harmful to the majority of bacteria (Ayre et al., 2017). As a result, the use of digestates as a substrate for microalgal growth opens the way for a variety of commercially feasible and ecologically acceptable applications, including biomethane and biofuel generation, as well as the creation of high added-value products such as PHA bioplastics (Koutra et al., 2018a). However, there is insufficient information available on the synthesis of PHB by microalgae grown in digestate. A recent study examined the cultivation of the cyanobacterium *Synechocystis salina* in digestate and reported the buildup of a PHB concentration of 6.3% (*w*/w) (P3HB) (Meixner et al., 2016). Nonetheless, growth of microalgae on digestate substrates warrants more investigation due to the presence of solids and possibly hazardous chemicals (Bauer et al., 2021; Xia and Murphy, 2016). Another significant inhibitor of microalgal growth is the increased turbidity of the digestate caused by suspended particles, which reduces the amount of photosynthetically active radiation (PAR) available to the culture (Bauer et al., 2021; Xia and Murphy, 2016). Table 3 summarizes the limited available published results regarding the production of bioplastics from microalgae cultivated in wastewater.

Microalgae biomass from wastewater should be collected to recover value-added bioproducts, including PHAs. The supply of light, optimum temperature maintenance, nutrients availability, the risk of contamination, the formation of biomass agglomerates and the oxygen accumulation from photosynthetic activity require control and standardization before the process can be considered applicable. The occasionally observed low growth rates of microalgae and cyanobacteria may be due either to the reduced illumination at specific spots of the cultures or to temperature changes in bioreactors. Also, the increase of oxygen in cultures does not favor the biological decomposition of carbon. Finally, the presence of nitrates in the substrate requires consumption of energy by the cells to convert them to ammonia, while the ammonia in the substrate can be toxic in high concentrations (Syahirah et al., 2021). Downstream processing, due to costs and practical difficulties, does not allow microalgae and cyanobacteria to be an important source of bioproducts, such as bioplastics. For the transition to pilot and industrial scale it is necessary to find and apply methods of recovery and separation that are environmentally friendly and economically viable as mentioned in Section 2.4 (Yashavanth et al., 2021).

2.4. Biopolymers extraction

In recent years, research has concentrated on developing extraction processes that will reduce the cost of bioplastics production. It is a general objective to develop extraction procedures that will provide a significant amount of bioplastics from microalgal biomass, while

Table 2
Comparison of physical properties of fossil-derived polymers to biopolymers that are produced by microalgae/cyanobacteria.

Polymer	T_m	T_g	Tensile strength (MPa)	Crystallinity (%)	Elongation at break (%)	Ref.
PP	176	-10	38	60	400	(Balaji et al., 2013; Hazer and Steinbüchel, 2007; Verlinden et al., 2007)
HDPE	129	–	–	70	12	(Costa et al., 2019)
LDPE	130	−30	10	–	620	(Khanna and Srivastava, 2005)
PHB	177	3	41.5	60	5.5	(Balaji et al., 2013; Koller et al., 2010; Verlinden et al., 2007)
PHBV	145	−1	20	56	50	(Balaji et al., 2013; Verlinden et al., 2007)
PHB4B	150	−7	26	45	444	(Balaji et al., 2013; Verlinden et al., 2007)
PHBHx	127	−1	21	34	400	(Balaji et al., 2013; Verlinden et al., 2007)
P4HB	56.5	−45	104	56	1000	(Hazer and Steinbüchel, 2007; Koller et al., 2010)
P(3HB-co-3 HV), cyanobacterium *Nostoc, muscorum Agardh*	152	−3	24.5	–	78.5	(Bhati and Mallick, 2012)
P(3HB-co-3 HV), cyanobacterium *Aulosira fertilissima*	161	−4.6	24	49	81	(Samantaray and Mallick, 2014)
PHB, cyanobacterium *Nostoc muscorum Agardh*	175	0.9	30.2	–	4.9	(Bhati and Mallick, 2012)

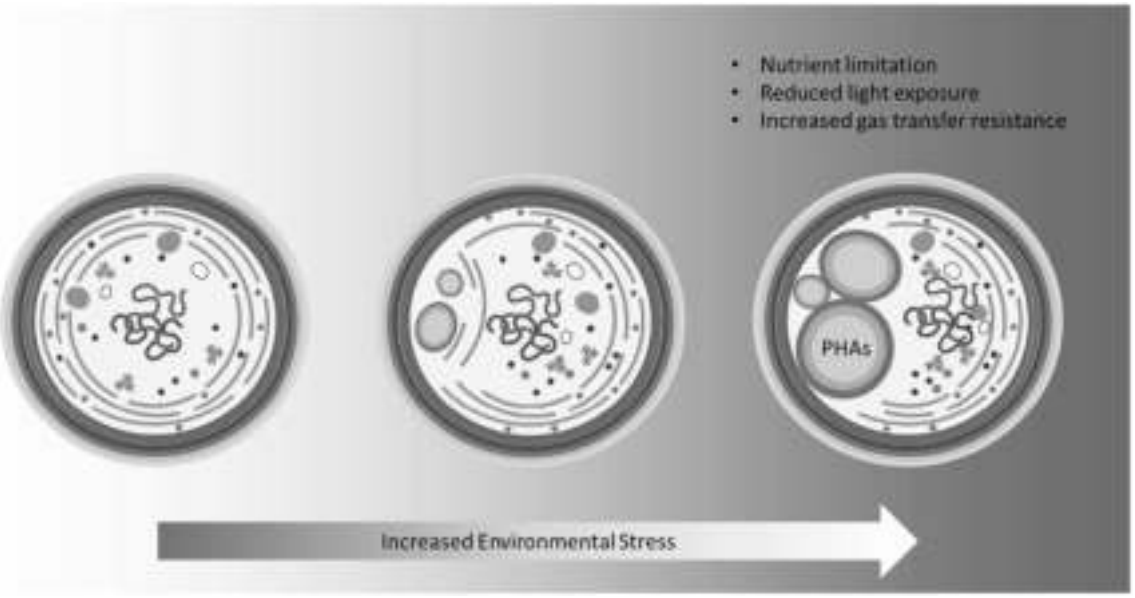

Fig. 3. Production of PHB from microalgae cultivated in wastewater.

Table 3
Published data regarding the production of bioplastics from microalgae cultivated in wastewater.

Strain	Growth media	PHB productivity	Nutrient removal efficiency	Ref.
Botryococcus braunii	60% sewage wastewater	247 mg L^{-1}	99.6% free ammonia, 81.8% nitrate, 45.0% phosphate,	(Kavitha et al., 2016)
Synechocystis sp. PCC 6803 strain ΔSphU	Shrimp wastewater	32.48% dcw	96.99% phosphate, 80.10% nitrate, 67.90% nitrite, 98.07% ammonium	(Krasaesueb et al., 2019)
Nostoc muscorum Agardh	10 g/L^{-1} Poultry litter	23.0% dcw, (144.2 mg L^{-1})	100% nitrite, 96–100% nitrate, 95–97% ammonium, 95–99% orthophosphate	(Bhati and Mallick, 2016)
	10 g/L^{-1} Poultry litter, +10% CO_2, +0.28% acetate +0.38% glucose, +0.30% valerate	65.0% dcw (773.5 mg L^{-1})	–	
Synechocystis salina	Digestate supernatant	1.6 g L − 1, 5.5% (w/w)	–	(Kovalcik et al., 2017)
	1/3 diluted low-solid digestate supernatant	88.7 mg L^{-1}, 5.5%	40% TN, >60% P	(Meixner et al., 2016)
B. braunii	50% palm oil mill effluent, 10 mg L^{-1} Fe- EDTA, 3 g L^{-1} glycerol	33% dcw	–	(Nur et al., 2021)

allowing for use of the leftover biomass. Since microalgae are a source of a range of important substances (proteins, fatty acids, and pigments), their co-production with PHA would increase the economic and environmental sustainability of such processes. The amount and quality of bioproducts are dictated not only by the biomass growing parameters, but also by the subsequent biorefinery methods. In the work of (Fei et al., 2016) it was reported that harsh extraction methods including high temperatures or strong acids could negatively affect the quality of the produced biopolymers. The existing research demonstrates that extraction efficiency is dependent on both the extraction technique used and the strain under investigation (Haddadi et al., 2019).

The most frequently used extraction methods are based on organic solvents and consist of three phases (Fig. 4). The first step is to dry the biomass. Removing moisture from biomass may be accomplished by freeze-drying or sun-drying and is crucial for the subsequent phases of the process that involve the use of organic solvents. Disruption of the cell membrane is the second stage in biopolymer extraction. This may be accomplished by the use of organic solvents or through the use of physical stress, such as sonication. The second stage enables mass transfer of the biopolymer from inside the cell to the bulk of the extraction solution introduced in the third step. The solvents chloroform, acetone, and dichloromethane are often employed because they dissolve biopolymers but not other biological products (Levett et al., 2016). After mixing the dry biomass with a suitable solvent and performing the extraction, another solvent, often methanol, is required for precipitation and recovery of the crystalline biopolymer (Kosseva and Rusbandi, 2018; Roja et al., 2019). While organic solvents generate a product with a low moisture content and do not significantly reduce the molecular weight of the polymer, they come at a high cost and have a negative influence on the environment (Kosseva and Rusbandi, 2018). As a result, new ecologically friendly and cost-effective technologies for scaling up bioplastic manufacturing are required.

Biomass digestion may be a viable option for recovering biopolymers. Hydrolysis of cells containing PHA occurs in an acidic or alkaline media, leaving the desired product insoluble. On the other hand, sulfuric acid and sodium hypochlorite, which are often employed to regulate the pH, seem to be detrimental to the recovered polymers, reducing their molecular weight and impairing the product's physicochemical characteristics (Fei et al., 2016). To prevent such effects, emphasis in biomass treatment has switched toward enzymes capable of denaturing the cell wall without degrading PHAs (Kapritchkoff et al.,

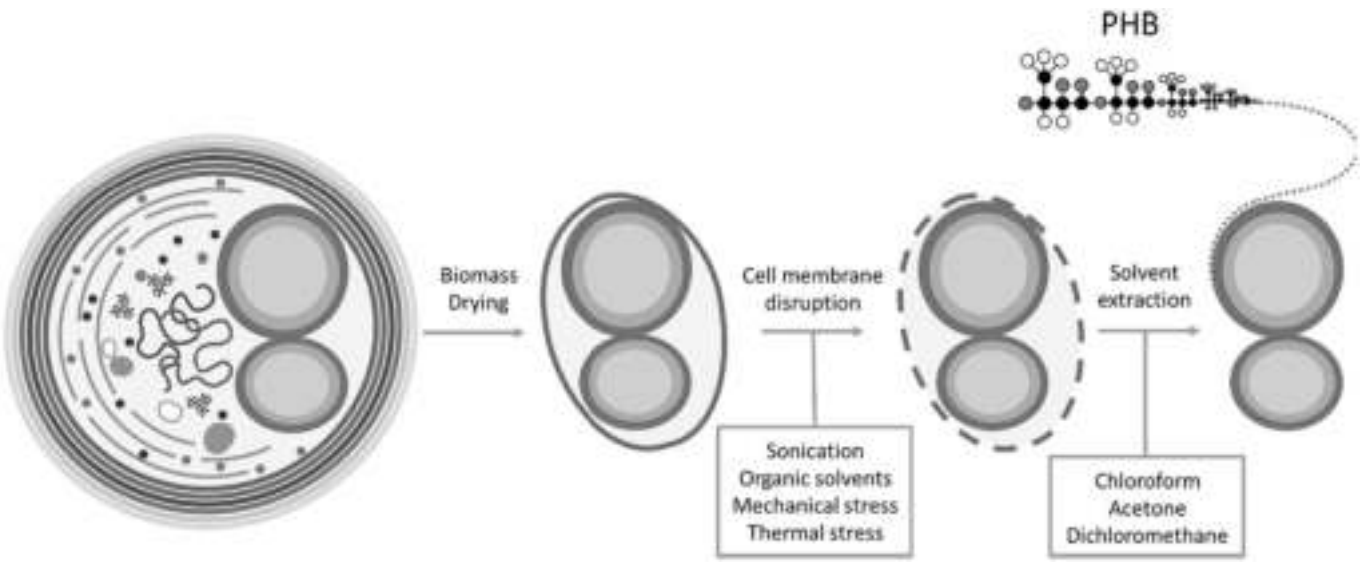

Fig. 4. Steps typically followed during biopolymer extraction from biomass.

2006; Poltronieri et al., 2016).

Another possibility for organic solvent-free extraction procedures is the use of supercritical fluids. The majority of reports indicate that supercritical carbon dioxide is employed for this purpose, extracting around 90% of the PHA content at purity levels of up to 99% (Gumel et al., 2013). Furthermore, an additional stage of supercritical carbon dioxide extraction may be used to purify the biopolymers by separating oily biomass residues at 150 bar and 50 °C (Daly et al., 2018). Despite the many positive findings published in the literature for extraction and purification utilizing supercritical fluids, the high operational costs associated with such methods restrict their widespread application.

Non-chlorinated solvents such as cyclohexanone and butyrolactone show significant promise in the area of non-toxic, eco-friendly solvents, since they perform as well as halogenated solvents at a lower cost. Although the extraction of PHB with cyclohexanone yields a significant PHA recovery, the process seems to be temperature sensitive (Jiang et al., 2018). Additionally, ionic liquids are recommended as extraction solvents with the aim of completely replacing organic solvents. Ionic liquids are solutions formed from salts that behave similarly to conventional organic solvents due to their electrically charged ions (Wang et al., 2017). At moderate temperatures, either wet or dry biomass may be treated with 1-Ethyl-3-methylimidazolium diethyl phosphate to recover up to 60% of biopolymer components. Additionally, it is highlighted that the ionic liquid may be recovered, hence increasing the process's feasibility (Dubey et al., 2018). Finally, Aqueous Two-Phase Extraction (ATPE) is a technique based on the formation of two separate phases comprising of either two distinct polymers or a polymer and an inorganic salt dissolved in water (Leong et al., 2017b). The temperature, concentration of dissolved compounds, and duration of the extraction all contribute to the bioplastics' recovery rate. Ethylene oxide-propylene oxide/sodium chloride, ethylene oxide-propylene oxide/ammonium sulfate, and polyethylene glycol/potassium phosphate are only a few of the combinations of dissolved substances in ATPEs that relate to PHA (Divyashree et al., 2009; Leong et al., 2017a, 2017b). Due to its nontoxicity and scalability at a low operating cost, this technology is deemed technically and economically viable both as the primary extraction process as well as a pretreatment step.

A biomass pretreatment phase is useful in the majority of biorefinery systems for bioplastics production because it boosts the biopolymer recovery rate and purity levels. The pretreatment approaches are designed to disrupt the physicochemical properties of the cells being employed and vary in terms of energy needs and efficiency. Cells may be broken down by applying shear stresses, which can be accomplished using a bead mill or a high-pressure homogenizer. Both procedures should be kept at a temperature close to 25 °C to avoid harming the extracted polymers (Madkour et al., 2013). Thermal pretreatment is also extensively used, since significant temperature fluctuations may disrupt cell membranes. Nonetheless, biomass heating may degrade the polymer's quality if the temperature and time are not adequately controlled; moreover, freezing-thawing cycles are energy intensive (Madkour et al., 2013). Additionally, cells may be broken down using sonication prior to PHA or PHB extraction. To increase the effectiveness of the ultrasound, the biomass is propagated in an ionic or nonionic surfactant. The use of sodium dodecyl sulfate (SDS) in sonication tests resulted in the extraction of a biopolymer with a purity of 96% (Arikawa et al., 2017). It was shown that pretreatment with sonication reduced the requirement for hazardous organic solvents, since biomass treated with sodium hypochlorite produced PHB with satisfactory properties (Martínez-Herrera et al., 2020). Nonionic surfactants such as polyoxymethylene sorbitan monolaurate may also increase PHA recovery, although chloroform and acidified methanol must be used to recover a pure product without considerable molecular weight decrease (Colombo et al., 2020).

2.5. Microalgal biomass blends

Bio-based polymer technologies are often expensive due to the extraction and purification phases required to produce a commercial product with the desired properties. While biorefinery processes incur large financial costs, they seldom result in a product that retains its thermal and mechanical qualities (Ivanov et al., 2014; Rujnić-Sokele and Pilipović, 2017). Today's market, places importance on high-quality polymers, such as those produced from fossil fuels, which contradicts with the environmental need for recyclable and biodegradable materials. Thus, attempts are being undertaken to develop plastics by combining biopolymers with a range of additives or even petroleum-derived polymeric chemicals (Soroudi and Jakubowicz, 2013). Blends are regarded as novel materials having distinct qualities, which are often more appealing than those of their constituents. Despite the enhanced nature of these new materials, concerns regarding their uniformity and biodegradability have been raised (Endres, 2017).

The need for homogeneity derives from the requirement for materials that are free of morphological defects and failures. Blending success is contingent on not just temperature, pressure, and processing time, but also on the compatibility of the components being combined. In the case of biopolymer blends, the source of the biomass (microorganism species and growth conditions) is equally critical. For example, when *Chlorella*

vulgaris and *Spirulina platensis* were investigated for biopolymer synthesis, the former displayed acceptable bioplastic characteristics, whilst the latter was shown to be more suited for blending with polyethylene (Zeller et al., 2013).

It is essential to pretreat cells containing polymers to get a homogenous material from biomass. Mechanical or chemical pretreatment is possible. Grinding biomass is critical for the formation of micro polymeric particles that can readily distribute throughout the bulk of the resulting mixture. The improved dispersion of biopolymers results in an increase in crystallinity, which impacts mechanical characteristics but decreases the final product's melting temperature (Simonic and Zemljic, 2020). Additionally, ultrasonication has been used prior to combining *Chlorella* biomass and PVA, resulting in a homogenous product with no surface imperfections. The sonication of the biomass resulted in the formation of a mixture with increased tensile strength and elongation capability (Sabathini et al., 2018). After ultrasonication, PVA was also combined with *Spirulina* biomass leftovers, resulting in a material with a tensile strength of 22 MPa and a break elongation of 77%. Water resistance was observed in the final product, which was attributable to the inorganic biomass components removed during ultrasonication (Zhang et al., 2020). Chemical procedures are often employed to remove non-polymerizable components from biomass washes (Jang et al., 2013). To rupture the cell wall of *Chlorella sorokiniana* and generate starch particles, ethanol was utilized as a cell suspension medium (Gifuni et al., 2017). If a colorless polymeric material is desired, methanol is an excellent solvent since it effectively eliminates undesirable biomass pigments (Monshupanee et al., 2016). Finally, low concentrations of either base or acid degraded cellular polysaccharides have been employed to generate monomers for the production of biopolymers with the aid of specialized enzymes such as cellulase (Naresh Kumar et al., 2020).

Polymer blends are formed within a mold at elevated temperatures and pressures. Both the parameters and duration of the procedure are regulated by the desired characteristics of the finished product. Initially, researchers used roller mixers to combine and shape bioplastics at elevated temperatures (Otsuki et al., 2004). However, the advancement of bioplastics manufacturing has facilitated the development of novel processes that have the potential to be utilized at a larger scale. When internal mixers were employed to produce bioplastic from maize starch and microalgal biomass, the species *Nannochloropsis gaditana* demonstrated exceptional flexibility and oxygen permeability (Fabra et al., 2018). Additionally, solvents may be utilized to cast polymeric composites if the proper ratio of components to dispersant is employed. Poly Vinyl Alcohol (PVA) was mixed with *Chlorella* biomass in the presence of glycerol and citric acid in distilled water, and the material characteristics were shown to be highly dependent on the biomass content (Sabathini et al., 2018). Screw extrusion and injection molding are also being tested in the field of bio-based mixes. Although these applications seem to be costly because of their energy consumption, they really increase blends production by reducing operational time and maintaining material uniformity (Mathiot et al., 2019; Torres et al., 2015). During the blending process, the binding between two polymeric compounds may be strengthened by the addition of compatibilizers or plasticizers. Compatibilizers are polymeric compounds that may stabilize a combination of two or more incompatible elements, transforming them into a homogeneous substance with enhanced properties. More precisely, compatibilizer particles are included into the bulk of the blend to minimize the interfacial tension between the incompatible components (Chen and White, 1993). On the other hand, plasticizers contribute to the mobility of polymer chains or act as an interfering agent between polymer bonds. As a result, a final polymeric mix that is both flexible and robust may be generated (Cadogan and Howick, 2001).

Numerous blends of polymers and biomass or biomass products have been produced and investigated for their thermal and mechanical properties throughout the years. PHB derived from biomass was studied in conjunction with polypropylene carbonate (PPC). The composites were deemed incompatible, and a compatibilizer, Poly Vinyl Acetate (PVAC), was introduced. As a consequence, the *co*-polymer's characteristics improved, but the degradation temperature and crystallization temperature decreased (Wang et al., 2005). Additionally, even at low concentrations, PP increased the durability of PHB by reducing its stiffness (Pachekoski et al., 2009). While *Nannochloropsis salina* improved the blend's thermal stability, it had a detrimental effect on the mechanical characteristics of PVA. The blend was homogenized and demonstrated a tensile strength of 20 MPa with the addition of Poly Diallyldimethylammonium chloride (PD) compatibilizer (Tran et al., 2016). PD improved the previously low values of elongation at break while increasing Young's modulus even further than pure PVA performance (Tran et al., 2016). Additionally, the blending capacity of *C. vulgaris* biomass with PVA was investigated. Maleic anhydrate and glycerol as a plasticizer were required in that study to create a high-quality polymer mixture. It was determined that the more compatibilizer, up to 5% by weight of PVA, was applied, the better the material performed in mechanical testing (Dianursanti, 2018).

A recent study on *Spirulina* biomass has focused on its compatibility with plastic blends. By combining *Spirulina* with non-biodegradable or slow-biodegradable polymers, it is possible to boost the final product's recyclability. Despite the plastic's reduced quality, *Spirulina* exhibited outstanding miscibility with PE. However, increasing the PE concentration increased the elongation rate of the blend (Zeller et al., 2013). Although Poly Butylene Succinate (PBS) is a biodegradable polymer with a similar profile to PP, *Spirulina* was utilized to investigate potential new materials (Zhu et al., 2017). Maleic anhydride was added as a compatibilizer, and both the tensile strength and Young's modulus increased. The compatibilizer, however, was unable to improve the poor elongation at break result. The final mixture crystallized at 73 °C and melted at 103 °C (Zhu et al., 2017). Additionally, *Spirulina* biomass was combined with PVA in a variety of ratios to create polymeric films, and glycerol was used to plasticize the films (Shi et al., 2017). Following film evaluation, it was determined that the PVA concentration resulted in increased tensile strength, while the glycerol component resulted in increased flexibility. Additionally, both PVA and glycerol were recognized as contributing to the manufacture of water-resistant recyclable films (Shi et al., 2017). Rather than that, water sensitivity developed as a result of mixing with wheat gluten, octanoic acid, and butanediol, despite the positive mechanical properties (Ciapponi et al., 2019). At the moment, efforts are being undertaken to combine *Spirulina* biomass with PLA without using compatibilizers. The newly created mixture exhibited higher crystallinity than pure PLA and demonstrated acceptable durability (Simonic and Zemljic, 2020).

3. Conclusions

Microalgae and cyanobacteria have been shown to be capable of generating bioplastics such as PHB as a means of storing energy and carbon when stressed. This has been proven by researchers even when microalgae/cyanobacteria were grown in wastewater, offering an environmentally benign source of nutrients. This is projected to drastically decrease bioplastics' carbon footprint and offer an eco-friendly alternative to petroleum-based plastics. Moreover, microalgae/cyanobacteria cultivation can lead to the recovery of high added-value products like pigments and antioxidants, promoting the economic viability of the process. Further research is required to refine and enhance the bioplastic recovery techniques used in order to minimize the usage of organic solvents and the process's overall environmental footprint. The downstream stage of the bioplastic manufacturing process may also have a significant impact on the final product's quality and, therefore, the applications for which it can be utilized. The gap between the characteristics of bioplastics and those of fossil-based plastics has been dramatically decreased, with bioplastics becoming increasingly suited for a wide variety of applications. A hybrid material, composed of a mixture of fossil-based plastics and algal biomass, has also been

proposed by researchers to produce materials with decreased environmental footprint and similar properties to conventional plastics. While it is true that bioplastics have a difficult time competing with the well-established usage of conventional plastics on a technological level, with the depletion of fossil fuels, climate change, and growing environmental consciousness, the tide seems to be turning in their favor.

Funding

This research has been co-financed by the European Union and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation 2014-2020 (EPAnEK)" in the context of the project entitled "ALGAVISION: Isolation and culture of local phytoplankton species aiming to mass production of antibacterial substances, fatty acids, pigments and antioxidants" (MIS 5048496).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Abdo, S.M., Ali, G.H., 2019. Analysis of polyhydroxybutrate and bioplastic production from microalgae. Bull. Natl. Res. Cent. 43 https://doi.org/10.1186/s42269-019-0135-5, 0–3.

Achilias, D.S., Roupakias, C., Megalokonomos, P., Lappas, A.A., Antonakou, V., 2007. Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). J. Hazard. Mater. 149, 536–542. https://doi.org/10.1016/j.jhazmat.2007.06.076.

Andrady, A.L., 2011. Microplastics in the marine environment. Mar. Pollut. Bull. 62, 1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030.

Ansari, S., Fatma, T., 2016. Cyanobacterial polyhydroxybutyrate (PHB): screening, optimization and characterization. PLoS One 11, 1–20. https://doi.org/10.1371/journal.pone.0158168.

Arikawa, H., Sato, S., Fujiki, T., Matsumoto, K., 2017. Simple and rapid method for isolation and quantitation of polyhydroxyalkanoate by SDS-sonication treatment. J. Biosci. Bioeng. 124, 250–254. https://doi.org/10.1016/j.jbiosc.2017.03.003.

Aydemir, D., Gardner, D.J., 2020. Biopolymer blends of polyhydroxybutyrate and polylactic acid reinforced with cellulose nanofibrils. Carbohydr. Polym. 250, 116867 https://doi.org/10.1016/j.carbpol.2020.116867.

Ayre, J.M., Moheimani, N.R., Borowitzka, M.A., 2017. Growth of microalgae on undiluted anaerobic digestate of piggery effluent with high ammonium concentrations. Algal Res. 24, 218–226. https://doi.org/10.1016/j.algal.2017.03.023.

Balaji, S., Gopi, K., Muthuvelan, B., 2013. A review on production of poly β hydroxybutyrates from cyanobacteria for the production of bio plastics. Algal Res. 2, 278–285. https://doi.org/10.1016/j.algal.2013.03.002.

Barsanti, L., Gualtieri, P., 2014. Algae: Anatomy, Biochemistry, and Biotechnology, Second Edition. CRC Press.

Bauer, L., Ranglová, K., Masojídek, J., Drosg, B., Meixner, K., 2021. Digestate as sustainable nutrient source for microalgae—challenges and prospects. Appl. Sci. 11, 1–21. https://doi.org/10.3390/app11031056.

Bhati, R., Mallick, N., 2012. Production and characterization of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) co-polymer by a N 2-fixing cyanobacterium, *Nostoc muscorum* Agardh. J. Chem. Technol. Biotechnol. 87, 505–512. https://doi.org/10.1002/jctb.2737.

Bhati, R., Mallick, N., 2015. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolymer production by the diazotrophic cyanobacterium Nostoc muscorum Agardh: process optimization and polymer characterization. Algal Res. 7, 78–85. https://doi.org/10.1016/j.algal.2014.12.003.

Bhati, R., Mallick, N., 2016. Carbon dioxide and poultry waste utilization for production of polyhydroxyalkanoate biopolymers by Nostoc muscorum Agardh: a sustainable approach. J. Appl. Phycol. 28, 161–168. https://doi.org/10.1007/s10811-015-0573-x.

Bjornsson, W.J., Nicol, R.W., Dickinson, K.E., McGinn, P.J., 2013. Anaerobic digestates are useful nutrient sources for microalgae cultivation: functional coupling of energy and biomass production. J. Appl. Phycol. 25, 1523–1528. https://doi.org/10.1007/s10811-012-9968-0.

Browne, M.A., 2013. Rochman 2013 Classify Plastic Waste as hazardous Nature 6–8.

Bugnicourt, E., Cinelli, P., Lazzeri, A., Alvarez, V., 2014. Polyhydroxyalkanoate (PHA): review of synthesis, characteristics, processing and potential applications in packaging. Express Polym Lett 8, 791–808. https://doi.org/10.3144/expresspolymlett.2014.82.

Cadogan, D.F., Howick, C.J., 2001. 1. Types of plasticizers. Encycl. Polym. Sci. Technol. 3 (3), 498–525.

Cassuriaga, A.P.A., Freitas, B.C.B., Morais, M.G., Costa, J.A.V., 2018. Innovative polyhydroxybutyrate production by Chlorella fusca grown with pentoses. Bioresour. Technol. 265, 456–463. https://doi.org/10.1016/j.biortech.2018.06.026.

Chen, C.C., White, J.L., 1993. Compatibilizing agents in polymer blends: interfacial tension, phase morphology, and mechanical properties. Polym. Eng. Sci. 33, 923–930. https://doi.org/10.1002/pen.760331409.

Chen, G.Q., Wu, Q., 2005. The application of polyhydroxyalkanoates as tissue engineering materials. Biomaterials 26, 6565–6578. https://doi.org/10.1016/j.biomaterials.2005.04.036.

Ciapponi, R., Turri, S., Levi, M., 2019. Mechanical reinforcement by microalgal biofiller in novel thermoplastic biocompounds from plasticized gluten. Materials (Basel). 12 https://doi.org/10.3390/ma12091476.

Colombo, B., Pereira, J., Martins, M., Torres-Acosta, M.A., Dias, A.C.R.V., Lemos, P.C., Ventura, S.P.M., Eisele, G., Alekseeva, A., Adani, F., Serafim, L.S., 2020. Recovering PHA from mixed microbial biomass: using non-ionic surfactants as a pretreatment step. Sep. Purif. Technol. 253 https://doi.org/10.1016/j.seppur.2020.117521.

Costa, S.S., Miranda, A.L., Andrade, B.B., Assis, D. de J., Souza, C.O., de Morais, M.G., Costa, J.A.V., Druzian, J.I., 2018a. Influence of nitrogen on growth, biomass composition, production, and properties of polyhydroxyalkanoates (PHAs) by microalgae. Int. J. Biol. Macromol. 116, 552–562. https://doi.org/10.1016/j.ijbiomac.2018.05.064.

Costa, J.A.V., Moreira, J.B., Lucas, B.F., Da Silva Braga, V., Cassuriaga, A.P.A., De Morais, M.G., 2018b. Recent advances and future perspectives of PHB production by cyanobacteria. Ind. Biotechnol. 14, 249–256. https://doi.org/10.1089/ind.2018.0017.

Costa, S.S., Miranda, A.L., de Morais, M.G., Costa, J.A.V., Druzian, J.I., 2019. Microalgae as source of polyhydroxyalkanoates (PHAs) — a review. Int. J. Biol. Macromol. 131, 536–547. https://doi.org/10.1016/j.ijbiomac.2019.03.099.

Cox, K.D., Covernton, G.A., Davies, H.L., Dower, J.F., Juanes, F., Dudas, S.E., 2019. Human consumption of microplastics. Environ. Sci. Technol. 53, 7068–7074. https://doi.org/10.1021/acs.est.9b01517.

Daly, S.R., Fathi, A., Bahramian, B., Manavitehrani, I., McClure, D.D., Valtchev, P., Schindeler, A., Dehghani, F., Kavanagh, J.M., 2018. A green process for the purification of biodegradable poly(B-hydroxybutyrate). J. Supercrit. Fluids 135, 84–90. https://doi.org/10.1016/j.supflu.2018.01.007.

Das, S.K., Sathish, A., Stanley, J., 2018. Production of biofuel and bioplastic from Chlorella Pyrenoidosa. Mater. Today Proc. 5, 16774–16781. https://doi.org/10.1016/j.matpr.2018.06.020.

Dianursanti, Gozan, M., Noviasari, C., 2018. The effect of glycerol addition as plasticizer in Spirulina platensis based bioplastic. E3S Web Conf. 67, 11–14. https://doi.org/10.1051/e3sconf/20186703048.

Divyashree, M.S., Shamala, T.R., Rastogi, N.K., 2009. Isolation of polyhydroxyalkanoate from hydrolyzed cells of Bacillus flexus using aqueous two-phase system containing polyethylene glycol and phosphate. Biotechnol. Bioprocess Eng. 14, 482–489. https://doi.org/10.1007/s12257-008-0119-z.

Domínguez-Díaz, M., Meneses-Acosta, A., Romo-Uribe, A., Peña, C., Segura, D., Espin, G., 2015. Thermo-mechanical properties, microstructure and biocompatibility in poly-β-hydroxybutyrates (PHB) produced by OP and OPN strains of Azotobacter vinelandii. Eur. Polym. J. 63, 101–112. https://doi.org/10.1016/j.eurpolymj.2014.12.002.

Dubey, S., Bharmoria, P., Gehlot, P.S., Agrawal, V., Kumar, A., Mishra, S., 2018. 1-Ethyl-3-methylimidazolium diethylphosphate based extraction of bioplastic "polyhydroxyalkanoates" from Bacteria: green and sustainable approach. ACS Sustain. Chem. Eng. 6, 766–773. https://doi.org/10.1021/acssuschemeng.7b03096.

Endres, H.-J., 2017. Large scale production of stem cells. Adv. Biochem. Eng. Biotechnol. 102, 1–35. https://doi.org/10.1007/10.

Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J., 2014. Plastic pollution in the World's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. PLoS One 9, 1–15. https://doi.org/10.1371/journal.pone.0111913.

European Bioplastics, 2017. Bioplastic market data 2017. Eur. Bioplastics 1–7.

Fabra, M.J., Martínez-Sanz, M., Gómez-Mascaraque, L.G., Gavara, R., López-Rubio, A., 2018. Structural and physicochemical characterization of thermoplastic corn starch films containing microalgae. Carbohydr. Polym. 186, 184–191. https://doi.org/10.1016/j.carbpol.2018.01.039.

Fang, S., Yu, W., Li, C., Liu, Y., Qiu, J., Kong, F., 2019. Adsorption behavior of three triazole fungicides on polystyrene microplastics. Sci. Total Environ. 691, 1119–1126. https://doi.org/10.1016/j.scitotenv.2019.07.176.

Fei, T., Cazeneuve, S., Wen, Z., Wu, L., Wang, T., 2016. Effective recovery of poly-β-hydroxybutyrate (PHB) biopolymer from *Cupriavidus necator* using a novel and environmentally friendly solvent system. Biotechnol. Prog. 32, 678–685. https://doi.org/10.1002/btpr.2247.

Galgani, F., Brien, A.S., Weis, J., Ioakeimidis, C., Schuyler, Q., Makarenko, I., Griffiths, H., Bondareff, J., Vethaak, D., Deidun, A., Sobral, P., Topouzelis, K., Vlahos, P., Lana, F., Hassellov, M., Gerigny, O., Arsonina, B., Ambulkar, A., Azzaro, M., Bebianno, M.J., 2021. Are litter, plastic and microplastic quantities increasing in the ocean? Microplastics and Nanoplastics 1, 8–11. https://doi.org/10.1186/s43591-020-00002-8.

Gifuni, I., Olivieri, G., Krauss, I.R., D'Errico, G., Pollio, A., Marzocchella, A., 2017. Microalgae as new sources of starch: isolation and characterization of microalgal starch granules. Chem. Eng. Trans. 57, 1423–1428. https://doi.org/10.3303/CET1757238.

Gironi, F., Piemonte, V., 2010. Bioplastics disposal: how to manage it. WIT Trans. Ecol. Environ. 140, 261–271. https://doi.org/10.2495/WM100241.

Gironi, F., Piemonte, V., 2011. Bioplastics and petroleum-based plastics: strengths and weaknesses. Energy sources. Part A Recover. Util. Environ. Eff. 33, 1949–1959. https://doi.org/10.1080/15567030903436830.

Gumel, A.M., Annuar, M.S.M., Chisti, Y., 2013. Recent advances in the production, recovery and applications of Polyhydroxyalkanoates. J. Polym. Environ. 21, 580–605. https://doi.org/10.1007/s10924-012-0527-1.

Haase, S.M., Huchzermeyer, B., Rath, T., 2012. PHB accumulation in *Nostoc muscorum* under different carbon stress situations. J. Appl. Phycol. 24, 157–162. https://doi.org/10.1007/s10811-011-9663-6.

Haddadi, M.H., Asadolahi, R., Negahdari, B., 2019. The bioextraction of bioplastics with focus on polyhydroxybutyrate: a review. Int. J. Environ. Sci. Technol. 16, 3935–3948. https://doi.org/10.1007/s13762-019-02352-0.

Hazer, B., Steinbüchel, A., 2007. Increased diversification of polyhydroxyalkanoates by modification reactions for industrial and medical applications. Appl. Microbiol. Biotechnol. 74, 1–12. https://doi.org/10.1007/s00253-006-0732-8.

Ivanov, V., Stabnikov, V., Ahmed, Z., Dobrenko, S., Saliuk, A., 2014. Production and applications of crude polyhydroxyalkanoate-containing bioplastic from the organic fraction of municipal solid waste. Int. J. Environ. Sci. Technol. 12, 725–738. https://doi.org/10.1007/s13762-014-0505-3.

Iwata, T., 2015. Biodegradable and bio-based polymers: future prospects of eco-friendly plastics. Angew. Chem. Int. Ed. 54, 3210–3215. https://doi.org/10.1002/anie.201410770.

Jang, Y.H., Han, S.O., Sim, I.N., Kim, H. Il, 2013. Pretreatment effects of seaweed on the thermal and mechanical properties of seaweed/polypropylene biocomposites. Compos. Part A Appl. Sci. Manuf. 47, 83–90. https://doi.org/10.1016/j.compositesa.2012.11.016.

Jiang, G., Johnston, B., Townrow, D.E., Radecka, I., Koller, M., Chaber, P., Adamus, G., Kowalczuk, M., 2018. Biomass extraction using non-chlorinated solvents for biocompatibility improvement of polyhydroxyalkanoates. Polymers (Basel). 10 https://doi.org/10.3390/polym10070731.

Kamravamanesh, D., Pflügl, S., Nischkauer, W., Limbeck, A., Lackner, M., Herwig, C., 2017. Photosynthetic poly-β-hydroxybutyrate accumulation in unicellular cyanobacterium Synechocystis sp. PCC 6714. AMB Express 7. https://doi.org/10.1186/s13568-017-0443-9.

Kapritchkoff, F.M., Viotti, A.P., Alli, R.C.P., Zuccolo, M., Pradella, J.G.C., Maiorano, A.E., Miranda, E.A., Bonomi, A., 2006. Enzymatic recovery and purification of polyhydroxybutyrate produced by Ralstonia eutropha. J. Biotechnol. 122, 453–462. https://doi.org/10.1016/j.jbiotec.2005.09.009.

Kaur, G., Wong, J.W.C., Kumar, R., Patria, R.D., Bhardwaj, A., Uisan, K., Johnravindar, D., 2020. Value addition of anaerobic digestate from biowaste: thinking beyond agriculture. Curr. Sustain. Energy Rep. 7, 48–55. https://doi.org/10.1007/s40518-020-00148-2.

Kavitha, G., Kurinjimalar, C., Sivakumar, K., Kaarthik, M., Aravind, R., Palani, P., Rengasamy, R., 2016. Optimization of polyhydroxybutyrate production utilizing waste water as nutrient source by Botryococcus braunii Kütz using response surface methodology. Int. J. Biol. Macromol. 93, 534–542. https://doi.org/10.1016/j.ijbiomac.2016.09.019.

Kavitha, G., Kurinjimalar, C., Sivakumar, K., Kaarthik, M., Aravind, R., Palani, P., Rengasamy, R., 2021. Optimization of polyhydroxybutyrate production utilizing waste water as nutrient source by *Botryococcus braunii* Kütz using response surface methodology. Int. J. Biol. Macromol. 93, 534–542.

Keshavarz, T., Roy, I., 2010. Polyhydroxyalkanoates: bioplastics with a green agenda. Curr. Opin. Microbiol. 13, 321–326. https://doi.org/10.1016/j.mib.2010.02.006.

Khanna, S., Srivastava, A.K., 2005. Recent advances in microbial polyhydroxyalkanoates. Process Biochem. 40, 607–619. https://doi.org/10.1016/j.procbio.2004.01.053.

Koller, M., Atlić, A., Dias, M., Reiterer, A., Braunegg, G., 2010. Microbial PHA Production from Waste Raw Materials, 14, pp. 85–119. https://doi.org/10.1007/978-3-642-03287-5_5.

Kosseva, M.R., Rusbandi, E., 2018. Trends in the biomanufacture of polyhydroxyalkanoates with focus on downstream processing. Int. J. Biol. Macromol. 107, 762–778. https://doi.org/10.1016/j.ijbiomac.2017.09.054.

Koutra, E., Economou, C.N., Tsafrakidou, P., Kornaros, M., 2018a. Bio-based products from microalgae cultivated in digestates. Trends Biotechnol. 36, 819–833. https://doi.org/10.1016/j.tibtech.2018.02.015.

Koutra, E., Grammatikopoulos, G., Kornaros, M., 2018b. Selection of microalgae intended for valorization of digestate from agro-waste mixtures. Waste Manag. 73, 123–129. https://doi.org/10.1016/j.wasman.2017.12.030.

Koutra, E., Mastropetros, S.G., Ali, S.S., Tsigkou, K., Kornaros, M., 2021. Assessing the potential of *Chlorella vulgaris* for valorization of liquid digestates from agro-industrial and municipal organic wastes in a biorefinery approach. J. Clean. Prod. 280, 124352 https://doi.org/10.1016/j.jclepro.2020.124352.

Kovalcik, A., Meixner, K., Mihalic, M., Zeilinger, W., Fritz, I., Fuchs, W., Kucharczyk, P., Stelzer, F., Drosg, B., 2017. Characterization of polyhydroxyalkanoates produced by *Synechocystis salina* from digestate supernatant. Int. J. Biol. Macromol. 102, 497–504. https://doi.org/10.1016/j.ijbiomac.2017.04.054.

Krasaesueb, N., Incharoensakdi, A., Khetkorn, W., 2019. Utilization of shrimp wastewater for poly-β-hydroxybutyrate production by Synechocystis sp. PCC 6803 strain ΔSphU cultivated in photobioreactor. Biotechnol. Reports 23, e00345. https://doi.org/10.1016/j.btre.2019.e00345.

Kwon, H.K., Jeon, J.Y., Oh, S.J., 2017. Potential for heavy metal (copper and zinc) removal from contaminated marine sediments using microalgae and light emitting diodes. Ocean Sci. J. 52, 57–66. https://doi.org/10.1007/s12601-017-0001-z.

Laycock, B., Halley, P., Pratt, S., Werker, A., Lant, P., 2013. The chemomechanical properties of microbial polyhydroxyalkanoates. Prog. Polym. Sci. 38, 536–583. https://doi.org/10.1016/j.progpolymsci.2012.06.003.

Leal Filho, W., Saari, U., Fedoruk, M., Iital, A., Moora, H., Klöga, M., Voronova, V., 2019. An overview of the problems posed by plastic products and the role of extended producer responsibility in Europe. J. Clean. Prod. 214, 550–558. https://doi.org/10.1016/j.jclepro.2018.12.256.

Lebreton, L., Andrady, A., 2019. Future scenarios of global plastic waste generation and disposal. Palgrave Commun. 5, 1–11. https://doi.org/10.1057/s41599-018-0212-7.

Lee, A., Liew, M.S., 2020. Ecologically derived waste management of conventional plastics. J. Mater. Cycles Waste Manag. 22, 1–10. https://doi.org/10.1007/s10163-019-00931-4.

Leong, Y.K., Lan, J.C.W., Loh, H.S., Ling, T.C., Ooi, C.W., Show, P.L., 2017a. Cloud-point extraction of green-polymers from *Cupriavidus necator* lysate using thermoseparating-based aqueous two-phase extraction. J. Biosci. Bioeng. 123, 370–375. https://doi.org/10.1016/j.jbiosc.2016.09.007.

Leong, Y.K., Show, P.L., Lan, J.C.W., Loh, H.S., Yap, Y.J., Ling, T.C., 2017b. Extraction and purification of Polyhydroxyalkanoates (PHAs): application of Thermoseparating aqueous two-phase extraction. J. Polym. Res. 24, 1–10. https://doi.org/10.1007/s10965-017-1307-3.

Leslie, H.A., van Velzen, M.J.M., Brandsma, S.H., Vethaak, A.D., Garcia-Vallejo, J.J., Lamoree, M.H., 2022. Discovery and quantification of plastic particle pollution in human blood. Environ. Int. 163, 107199 https://doi.org/10.1016/j.envint.2022.107199.

Levett, I., Birkett, G., Davies, N., Bell, A., Langford, A., Laycock, B., Lant, P., Pratt, S., 2016. Techno-economic assessment of poly-3-hydroxybutyrate (PHB) production from methane - the case for thermophilic bioprocessing. J. Environ. Chem. Eng. 4, 3724–3733. https://doi.org/10.1016/j.jece.2016.07.033.

Madkour, M.H., Heinrich, D., Alghamdi, M.A., Shabbaj, I.I., Steinbuchel, A., 2013. PHA recovery from biomass. Biomacromolecules 14 (9), 2963–2972. https://doi.org/10.1021/bm4010244.

Mahishi, L.H., Tripathi, G., Rawal, S.K., 2003. Poly(3-hydroxybutyrate) (PHB) synthesis by recombinant *Escherichia coli* harbouring *Streptomyces aureofaciens* PHB biosynthesis genes: effect of various carbon and nitrogen sources. Microbiol. Res. 158, 19–27. https://doi.org/10.1078/0944-5013-00161.

Mallick, N., Gupta, S., Panda, B., Sen, R., 2007. Process optimization for poly(3-hydroxybutyrate-co-3-hydroxyvalerate) co-polymer production by Nostoc muscorum. Biochem. Eng. J. 37, 125–130. https://doi.org/10.1016/j.bej.2007.04.002.

Markl, E., Grünbichler, H., Lackner, M., 2019. Cyanobacteria for PHB Bioplastics production: a review. Algae 1–10. https://doi.org/10.5772/intechopen.81536.

Markou, G., Nerantzis, E., 2013. Microalgae for high-value compounds and biofuels production: a review with focus on cultivation under stress conditions. Biotechnol. Adv. 31, 1532–1542. https://doi.org/10.1016/j.biotechadv.2013.07.011.

Martínez-Herrera, R.E., Alemán-Huerta, M.E., Almaguer-Cantú, V., Rosas-Flores, W., Martínez-Gómez, V.J., Quintero-Zapata, I., Rivera, G., Rutiaga-Quiñones, O.M., 2020. Efficient recovery of thermostable polyhydroxybutyrate (PHB) by a rapid and solvent-free extraction protocol assisted by ultrasound. Int. J. Biol. Macromol. 164, 771–782. https://doi.org/10.1016/j.ijbiomac.2020.07.101.

Martins, R.G., Severo Gonçalves, I., De Morais, M.G., Costa, J.A.V., 2014. Bioprocess engineering aspects of biopolymer production by the cyanobacterium spirulina strain LEB 18. Int. J. Polym. Sci. 2014, 1–7. https://doi.org/10.1155/2014/895237.

Martins, R.G., Gonçalves, I.S., De Morais, M.G., Vieira Costa, J.A., 2017. New technologies from the bioworld: selection of biopolymer-producing microalgae. Polimeros 27, 285–289. https://doi.org/10.1590/0104-1428.2375.

Mat Aron, N.S., Khoo, K.S., Chew, K.W., Show, P.L., Chen, W.H., Nguyen, T.H.P., 2020. Sustainability of the four generations of biofuels – a review. Int. J. Energy Res. 44, 9266–9282. https://doi.org/10.1002/er.5557.

Mathiot, C., Ponge, P., Gallard, B., Sassi, J.F., Delrue, F., Le Moigne, N., 2019. Microalgae starch-based bioplastics: screening of ten strains and plasticization of unfractionated microalgae by extrusion. Carbohydr. Polym. 208, 142–151. https://doi.org/10.1016/j.carbpol.2018.12.057.

Meixner, K., Fritz, I., Daffert, C., Markl, K., Fuchs, W., Drosg, B., 2016. Processing recommendations for using low-solids digestate as nutrient solution for poly-ß-hydroxybutyrate production with *Synechocystis salina*. J. Biotechnol. 240, 61–67. https://doi.org/10.1016/j.jbiotec.2016.10.023.

Mendhulkar, V.D., Shetye, L.A., 2017. Synthesis of biodegradable polymer polyhydroxyalkanoate (PHA) in cyanobacteria *Synechococcus elongates* under mixotrophic nitrogen- and phosphate-mediated stress conditions. Ind. Biotechnol. 13, 85–93. https://doi.org/10.1089/ind.2016.0021.

Monshupanee, T., Nimdach, P., Incharoensakdi, A., 2016. Two-stage (photoautotrophy and heterotrophy) cultivation enables efficient production of bioplastic poly-3-hydroxybutyrate in auto-sedimenting cyanobacterium. Sci. Rep. 6, 1–9. https://doi.org/10.1038/srep37121.

Możejko-Ciesielska, J., Kiewisz, R., 2016. Bacterial polyhydroxyalkanoates: still fabulous? Microbiol. Res. 192, 271–282. https://doi.org/10.1016/j.micres.2016.07.010.

Muneer, F., Rasul, I., Azeem, F., Siddique, M.H., Zubair, M., Nadeem, H., 2020. Microbial Polyhydroxyalkanoates (PHAs): efficient replacement of synthetic polymers. J. Polym. Environ. 28, 2301–2323. https://doi.org/10.1007/s10924-020-01772-1.

Naresh Kumar, A., Chatterjee, S., Hemalatha, M., Althuri, A., Min, B., Kim, S.H., Venkata Mohan, S., 2020. Deoiled algal biomass derived renewable sugars for bioethanol and biopolymer production in biorefinery framework. Bioresour. Technol. 296, 122315 https://doi.org/10.1016/j.biortech.2019.122315.

Nishioka, M., Nakai, K., Miyake, M., Asada, Y., Taya, M., 2001. Production of poly-β-hydroxybutyrate by thermophilic cyanobacterium, Synechococcus sp. MA19, under phosphate-limited conditions. Biotechnol. Lett. 23, 1095–1099. https://doi.org/10.1023/A:1010551614648.

Nur, M.M.A., Yuliestyan, A., Irfandy, F., Setyoningrum, T.M., 2021. Nutritional factors influence polyhydroxybutyrate in microalgae growing on palm oil mill effluent. J. Appl. Phycol. https://doi.org/10.1007/s10811-021-02654-2.

Otsuki, J., Zhang, F., Kabeya, H., Hirotsu, T., 2004. Synthesis and tensile properties of a novel composite of chlorella and polyethylene. J. Appl. Polym. Sci. 92, 812–816. https://doi.org/10.1002/app.13650.

Pachekoski, W.M., Agnelli, J.A.M., Belem, L.P., 2009. Thermal, mechanical and morphological properties of poly (hydroxybutyrate) and polypropylene blends after processing. Mater. Res. 12, 159–164. https://doi.org/10.1590/S1516-14392009000200008.

Panda, B., Jain, P., Sharma, L., Mallick, N., 2006. Optimization of cultural and nutritional conditions for accumulation of poly-β-hydroxybutyrate in Synechocystis sp. PCC 6803. Bioresour. Technol. 97, 1296–1301. https://doi.org/10.1016/j.biortech.2005.05.013.

Plastics Europe, G.M.R., 2019. Conversio market & strategy GmbH, 2019. Plastics - the Facts 14, 35.

Poltronieri, P., Mezzolla, V., D'Urso, O.F., 2016. PHB production in Biofermentors assisted through biosensor applications. Proceedings 1, 4. https://doi.org/10.3390/ecsa-3-e014.

Porras, M.A., Villar, M.A., Cubitto, M.A., 2017. Novel spectrophotometric technique for rapid determination of extractable PHA using Sudan black dye. J. Biotechnol. 255, 28–32. https://doi.org/10.1016/j.jbiotec.2017.06.012.

Ragusa, A., Svelato, A., Santacroce, C., Catalano, P., Notarstefano, V., Carnevali, O., Papa, F., Rongioletti, M.C.A., Baiocco, F., Draghi, S., D'Amore, E., Rinaldo, D., Matta, M., Giorgini, E., 2021. Plasticenta: first evidence of microplastics in human placenta. Environ. Int. 146, 106274 https://doi.org/10.1016/j.envint.2020.106274.

Rahman, M.H., Bhoi, P.R., 2021. An overview of non-biodegradable bioplastics. J. Clean. Prod. 294 https://doi.org/10.1016/j.jclepro.2021.126218.

Rahman, A., Ellis, J.T., Miller, C.D., 2012. Bioremediation of domestic wastewater and production of bioproducts from microalgae using waste stabilization ponds. J. Bioremediation Biodegrad. 03 https://doi.org/10.4172/2155-6199.1000e113.

Rahman, A., Miller, C.D., 2017. Microalgae as a Source of Bioplastics, Algal Green Chemistry: Recent Progress in Biotechnology. Elsevier B.V. https://doi.org/10.1016/B978-0-444-63784-0.00006-0.

Razza, F., Innocenti, F.D., 2012. Bioplastics from renewable resources: the benefits of biodegradability. Asia-Pacific J. Chem. Eng. 7, S301–S309. https://doi.org/10.1002/apj.1648.

Richmond, A., 2004. Handbook of microalgal culture: biotechnology and applied phycology, 1st Edition. Blackwell Science Ltd.

Rizwan, M., Mujtaba, G., Memon, S.A., Lee, K., Rashid, N., 2018. Exploring the potential of microalgae for new biotechnology applications and beyond: a review. Renew. Sust. Energ. Rev. 92, 394–404. https://doi.org/10.1016/j.rser.2018.04.034.

Rochman, C.M., Hoh, E., Hentschel, B.T., Kaye, S., 2013. Classify plastic waste as hazardous (types of externalities caused by consumption of plastic bags). Environ. Sci. Technol. 47, 1646–1654.

Roja, K., Ruben Sudhakar, D., Anto, S., Mathimani, T., 2019. Extraction and characterization of polyhydroxyalkanoates from marine green alga and cyanobacteria. Biocatal. Agric. Biotechnol. 22, 101358 https://doi.org/10.1016/j.bcab.2019.101358.

Roohi, Zaheer, M.R., Kuddus, M., 2018. PHB (poly-β-hydroxybutyrate) and its enzymatic degradation. Polym. Adv. Technol. 29, 30–40. https://doi.org/10.1002/pat.4126.

Rujnić-Sokele, M., Pilipović, A., 2017. Challenges and opportunities of biodegradable plastics: a mini review. Waste Manag. Res. 35, 132–140. https://doi.org/10.1177/0734242X16683272.

Sabathini, H.A., Windiani, L., Dianursanti, Gozan, M., 2018. Mechanical physicial properties of chlorella-PVA based bioplastic with ultrasonic homogenizer. E3S Web Conf. 67, 3–7. https://doi.org/10.1051/e3sconf/20186703046.

Samantaray, S., Mallick, N., 2014. Production of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) co-polymer by the diazotrophic cyanobacterium Aulosira fertilissima CCC 444. J. Appl. Phycol. 26, 237–245. https://doi.org/10.1007/s10811-013-0073-9.

Samantaray, S., Mallick, N., 2015. Impact of various stress conditions on poly-β-Hydroxybutyrate (PHB) accumulation in Aulosira fertilissima CCC 444. Curr. Biotechnol. 4, 366–372. https://doi.org/10.2174/2211550104666150806000642.

Sharma, V., Sehgal, R., Gupta, R., 2021. Polyhydroxyalkanoate (PHA): properties and modifications. Polymer (Guildf). 212, 123161 https://doi.org/10.1016/j.polymer.2020.123161.

Shi, B., Liang, L., Yang, H., Zhang, L., He, F., 2017. Glycerol-plasticized spirulina–poly (vinyl alcohol) films with improved mechanical performance. J. Appl. Polym. Sci. 134, 1–10. https://doi.org/10.1002/app.44842.

Simonazzi, M., Pezzolesi, L., Galletti, P., Gualandi, C., Pistocchi, R., De Marco, N., Paganelli, Z., Samorì, C., 2021. Production of polyhydroxybutyrate by the cyanobacterium cf. Anabaena sp. Int. J. Biol. Macromol. 191, 92–99. https://doi.org/10.1016/j.ijbiomac.2021.09.054.

Simonic, M., Zemljic, F., 2020. Production of bioplastic material from algal biomass. Chem. Ind. Chem. Eng. Q. 26–26 https://doi.org/10.2298/ciceq191024026s.

Singh, A.K., Sharma, L., Mallick, N., Mala, J., 2017. Progress and challenges in producing polyhydroxyalkanoate biopolymers from cyanobacteria. J. Appl. Phycol. 29, 1213–1232. https://doi.org/10.1007/s10811-016-1006-1.

Singh, M.K., Rai, P.K., Rai, A., Singh, S., Singh, J.S., 2019. Poly-β-hydroxybutyrate production by the cyanobacterium scytonema geitleri bharadwaja under varying environmental conditions. Biomolecules 9, 1–10. https://doi.org/10.3390/biom9050198.

Soroudi, A., Jakubowicz, I., 2013. Recycling of bioplastics, their blends and biocomposites: a review. Eur. Polym. J. 49, 2839–2858. https://doi.org/10.1016/j.eurpolymj.2013.07.025.

Spain, O., Plöhn, M., Funk, C., 2021. The cell wall of green microalgae and its role in heavy metal removal. Physiol. Plant. 1–10 https://doi.org/10.1111/ppl.13405.

Sudesh, K., Taguchi, K., Doi, Y., 2002. Effect of increased PHA synthase activity on polyhydroxyalkanoates biosynthesis in Synechocystis sp. PCC6803. Int. J. Biol. Macromol. 30, 97–104. https://doi.org/10.1016/S0141-8130(02)00010-7.

Syahirah, N., Aron, M., Shiong, K., Wayne, K., Veeramuthu, A., Chang, J., Loke, P., 2021. Microalgae cultivation in wastewater and potential processing strategies using solvent and membrane separation technologies. J. Water Process Eng. 39, 101701 https://doi.org/10.1016/j.jwpe.2020.101701.

Toh, P.S., Jau, M.H., Yew, S.P., Abed, R.M., Sudesh, K., 2008. Comparison of Polyhydroxyalkanoates biosynthesis, mobilization and the effects on cellular morphology in Spirulina platensis and Synechocystis Sp. Uniwg. J. Biosci. 19, 21–38.

Torres, S., Navia, R., Campbell Murdy, R., Cooke, P., Misra, M., Mohanty, A.K., 2015. Green composites from residual microalgae biomass and poly(butylene adipate-co-terephthalate): processing and plasticization. ACS Sustain. Chem. Eng. 3, 614–624. https://doi.org/10.1021/sc500753h.

Tran, D., Lee, H.R., Jung, S., Park, M.S., Yang, J., 2016. Lipid-extracted algal biomass based biocomposites fabrication with poly (vinyl alcohol). ALGAL. https://doi.org/10.1016/j.algal.2016.08.016.

Van Eygen, E., Feketitsch, J., Laner, D., Rechberger, H., Fellner, J., 2017. Comprehensive analysis and quantification of national plastic flows: the case of Austria. Resour. Conserv. Recycl. 117, 183–194. https://doi.org/10.1016/j.resconrec.2016.10.017.

Vanessa, C.C., Cleber, K. da S., Ana, L.T., Jorge, A.V.C., Michele, G. de M., 2015. Polyhydroxybutyrate production by Spirulina sp. LEB 18 grown under different nutrient concentrations. Afr. J. Microbiol. Res. 9, 1586–1594. https://doi.org/10.5897/ajmr2015.7530.

Verlinden, R.A.J., Hill, D.J., Kenward, M.A., Williams, C.D., Radecka, I., 2007. Bacterial synthesis of biodegradable polyhydroxyalkanoates. J. Appl. Microbiol. 102, 1437–1449. https://doi.org/10.1111/j.1365-2672.2007.03335.x.

Wang, X., Peng, S., Dong, L., 2005. Effect of poly(vinyl acetate) (PVAc) on thermal behavior and mechanical properties of poly(3-hydroxybutyrate)/poly(propylene carbonate) (PHB/ PPC) blends. Colloid Polym. Sci. 284, 167–174. https://doi.org/10.1007/s00396-005-1353-y.

Wang, B., Qin, L., Mu, T., Xue, Z., Gao, G., 2017. Are ionic liquids chemically stable? Chem. Rev. 117, 7113–7131. https://doi.org/10.1021/acs.chemrev.6b00594.

Xia, A., Murphy, J.D., 2016. Microalgal cultivation in treating liquid digestate from biogas systems. Trends Biotechnol. 34, 264–275. https://doi.org/10.1016/j.tibtech.2015.12.010.

Yashavanth, P.R., Das, M., Maiti, S.K., 2021. Recent progress and challenges in cyanobacterial autotrophic production of polyhydroxybutyrate (PHB), a bioplastic. J. Environ. Chem. Eng. 9.

Zeller, M.A., Hunt, R., Jones, A., Sharma, S., 2013. Bioplastics and their thermoplastic blends from Spirulina and Chlorella microalgae. J. Appl. Polym. Sci. 130, 3263–3275. https://doi.org/10.1002/app.39559.

Zhang, S., Bryant, D.A., 2015. Biochemical validation of the glyoxylate cycle in the cyanobacterium *Chlorogloeopsis fritschii* strain PCC 9212. J. Biol. Chem. 290, 14019–14030. https://doi.org/10.1074/jbc.M115.648170.

Zhang, C., Wang, C., Cao, G., Wang, D., Ho, S.H., 2020. A sustainable solution to plastics pollution: an eco-friendly bioplastic film production from high-salt contained Spirulina sp. residues. J. Hazard. Mater. 388, 121773 https://doi.org/10.1016/j.jhazmat.2019.121773.

Zhu, N., Ye, M., Shi, D., Chen, M., 2017. Reactive compatibilization of biodegradable poly(butylene succinate)/Spirulina microalgae composites. Macromol. Res. 25, 165–171. https://doi.org/10.1007/s13233-017-5025-9.