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# Chapter 11

# Production of biopolymers from microalgae and cyanobacteria

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**ABSTRACT**

Over the past few decades, plastic-derived pollution has been recognized as a major environmental issue because the use of conventional plastics results in vast amounts of waste as well as in fossil-fuel depletion. Biodegradable and biobased polymers are a promising alternative to conventional plastics. In this context, polyhydroxyalkanoates (PHAs) are bioplastics with similar mechanical and thermal properties to petroleum-based plastics which can be used in a wide range of applications. Several studies have reported the accumulation of PHAs in the biomass of microalgae and cyanobacteria. Under optimal conditions for PHA accumulation, that is, nutrient limitation, and optimal light intensity, PHA content can significantly increase, achieving 85% of dry biomass weight. Downstream recovery of PHAs is also a critical step that affects the properties and the yield of PHAs. Bioplastic production from microalgae and cyanobacteria on a commercial scale is still limited due to its high cost, with the cultivation medium accounting for up to 50% of the total production cost. The use of wastewater as a growth medium can improve the economic feasibility and sustainability of PHA production from microalgae and cyanobacteria and contribute to a more circular economy.

**Keywords:** biodegradable bioplastics, bioplastic recovery, biorefinery, cyanobacteria, downstream processing, microalgae, PHA blends, polyhydroxyalkanoates, sustainability, upstream processing, wastewater.

## 11.1 INTRODUCTION

Plastic has made our lives more convenient. This increased convenience has led to an increase in demand, which, in turn, caused an exponential increase in the production of plastics since the beginning of their industrial production, resulting in ~8 billion tons of plastic generated from 1950 onward (European Environmental Agency, 2020). The annual production of plastics steadily increases at a yearly average of 4%, from 279 million tons in 2011 to 391 million tons in 2021 (Statista, 2023). Plastics are polymeric substances, the properties of which depend on the structure of individual monomers and range from flexible to stiff, from permeable to impermeable, from hydrophilic to hydrophobic. Conventional plastics are derived from fossil-based chemicals, and are a cheap solution for strong and durable materials. Commonly used plastics include polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polyvinyl chloride, polystyrene (PS), and polyamides (nylons), and are constituents of a wide variety of products, including medical equipment, agricultural tools, electronic devices, and packaging (Leal Filho *et al.*, 2019).

The unblemished optimism regarding plastics changed around the 1970s. Due to their short usable life and their non-biodegradable nature, the accumulation of plastic in the environment became hard to miss, thereby damaging their reputation (Carpenter & Smith, 1972). From then on, the view on plastics has drastically changed. It is now well-known that due to their long lifetime, for instance up to 800 years as the average reported lifetime for PET (Ward & Reddy, 2020), plastics accumulate in the environment if not properly handled. In more tangible terms, estimations show that the primary plastic waste generation amounted to ~7,500 million tons in 2020, whereas over 200,000 tons of plastic waste enter the Mediterranean Sea every year (European Environmental Agency, 2020), with an economic cost ranging between \$3,300 and \$33,000 per ton marine plastics per year (Beaumont *et al.*, 2019). When improperly disposed of in the environment, plastics break into small insoluble pieces, referred to as microplastics (with diameters between 1 μm and 5 mm), the size of which makes them difficult to track, trace, and remove (Tirkey & Upadhyay, 2021). Microplastics have thereby entered the food chain (especially via marine animals) and are even found in women's placentas (Ragusa *et al.*, 2021). In addition to this repulsive fact, plastic production consumes ~6% of the global crude oil supply and is responsible for the generation of 2% of the global carbon dioxide ($CO_2$) emissions (Rosenboom *et al.*, 2022). Therefore, apart from the global health, it is crucial to pursue alternative solutions that also tackle the environmental impact. All these facts call for drastic changes regarding the generation, use, and disposal of plastics.

Biobased bioplastics, polymers derived from biological sources, can be a more sustainable alternative to conventional plastics (European Bioplastics, 2018). They can be divided into two categories, namely (1) biodegradable, for example, polylactic acid (PLA) derived from lactic acid, polyhydroxyalkanoates (PHAs), cellulose, and starch-based bioplastics, and (2) non-biodegradable, such as organic PE and PET (Rosenboom *et al.*, 2022). Advantages of bioplastics over conventional plastics include improved circularity due to the use of renewable resources, lower environmental footprint, biodegradation, and improved properties, which depend on the specific bioplastic type (Rosenboom *et al.*, 2022). Life-cycle assessments show that the substitution of conventional plastics with bioplastics, even from first-generation biofuels, requires 86% less non-renewable energy (Singh *et al.*, 2022). The production of fully biobased bioplastics is currently estimated at ~2 million tons per year (Chen, 2019), and they are expected to play a key role in future circular economy (Cheng & Gross, 2020). In this context, the biomass of microorganisms is increasingly gaining interest as a raw material for biobased products such as bioplastics. Microalgae and cyanobacteria are two microbial groups that have gained a significant share of the attention for this application, due to their potential bioplastic production from recovered resources such as nutrients and organics from wastewater, or $CO_2$ from off-gasses as well as their high content in targeted biopolymer precursors (Mastropetros *et al.*, 2022).

## 11.2 STRUCTURE AND PROPERTIES OF BIODEGRADABLE BIOPLASTICS

Biodegradable bioplastics include a range of materials derived from biological processes such as agriculture-derived polysaccharides (e.g., starch- and cellulose-based bioplastics) (Abe *et al.*, 2021), microbial fermentation products (e.g., lactic acid for PLA), and intracellular microbial components (e.g., PHAs), while the feasibility of converting the whole microbial biomass into bioplastic composites has recently been shown as well (Singha *et al.*, 2021). Starch- and cellulose-based bioplastics are interesting due to their abundance, affordability, durability, strength, and biodegradability (Abe *et al.*, 2021; Nanda *et al.*, 2022). Even though cellulose-based biopolymers are water-sensitive and lack interfacial adhesion and thermal stability, research shows that pretreatment can overcome these challenges and increase the popularity of these polymers (Polman *et al.*, 2021). Applications of cellulose-based polymers include packaging films, frames for eyeglasses, and food packaging (Nanda *et al.*, 2022). Starch-based polymers are considered to be promising to produce edible films and have similar mechanical properties and transparency to conventional polymers (Shahabi-Ghahfarrokhi *et al.*, 2019). Similar to cellulose-based polymers, starch-based polymers are also sensitive to moisture, do not have optimal mechanical properties and thermal stability, are gas permeable, and have odor issues (Nanda *et al.*, 2022; Toh *et al.*, 2008). However, combination with other polymers, essential oils, fibers, or plasticizers improves their properties (Syafiq *et al.*, 2020), and enables applications in food-packaging and pharmaceutical fields. Lactic acid monomers are further polymerized to yield PLA, a non-toxic, biocompatible polymer with mechanical properties similar to PET and PS (Karamanlioglu *et al.*, 2017). Owing to its stiffness, mechanical strength, flexibility, thermal stability, lower temperature heat sealing ability, aroma, and flavor resistance, PLA finds applications, among others in food packaging, agriculture, transportation, furniture, electronic appliances, and fabrics (Jamshidian *et al.*, 2010). Finally, the versatility and durability of PHAs has placed them in the spotlight, and their market is increasing, with projections showing an increase from 81 million USD in 2022 to 167 million USD in 2027 (Markets and Markets, 2022).

Microalgae and cyanobacteria produce various types of PHAs, including polyhydroxybutyrate (PHB), poly-3-hydroxybutyrate (P(3HB)), and co-polymers such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) (Mastropetros *et al.*, 2022). These PHAs have properties comparable to conventional plastics such as PP and PE and find applications in the food and bulk-packaging sectors. Furthermore, due to their high biocompatibility and complete biodegradability, they can have high-value applications in the biomedical sector (Costa *et al.*, 2019; Koller, 2018; Paulraj *et al.*, 2018). PHB, the most prevalent PHAs, has a higher melting point and a comparable tensile strength compared to PP and PS (Khanna & Srivastava, 2005). Nevertheless, the low flexibility (i.e., elongation at break), and high brittleness and crystallinity limit the potential applications, excluding their conversion to durable materials (Muneer *et al.*, 2020). Especially regarding crystallinity, levels above 50% yield brittle polymers and are therefore undesirable (Laycock *et al.*, 2013), with microalgal and cyanobacterial PHAs approaching this range (Table 11.1). Additionally, the temperature at which PHB undergoes thermal degradation is very close to its melting point, which causes failures in many applications (Aydemir & Gardner, 2020). Therefore, medium-chain PHA (6–14 carbon atoms) or co-polymers are preferred because they present improved properties (Table 11.1). These properties are correlated with the molecular weight and structure of the monomers (Bugnicourt *et al.*, 2014), the composition of which is determined by the genetic potential of the microorganisms to produce them. Nevertheless, common chemical modification methods have been shown to improve the properties of these microalgal and cyanobacterial PHAs and are recommended to improve the properties and increase the number of applications.

Microalgae and cyanobacteria that are able to produce PHAs have been recently reviewed and summarized by Mastropetros *et al.* (2022), and species with the highest content (up to 78%) belong to the genera *Arthrospira* sp., *Synechocystis* sp., *Synechococcus* sp., *Nostoc* sp., and *Anabaena* sp. Importantly, microalgal and cyanobacterial PHAs can be produced on side-streams, further increasing their sustainability. Despite their good prospects, currently there are only a limited number of studies that show the feasibility of this concept and test the properties of microalgae- and cyanobacterial-derived PHAs, which will be discussed in the following sections.

## 11.3 EMPLOYING MICROALGAE AND CYANOBACTERIA FOR BIOPLASTIC PRODUCTION

Among the different types of bioplastics currently considered as more sustainable alternatives to conventional plastics, biodegradable and biobased PHAs are considered to be a promising solution

**Table 11.1** Average physical properties of conventional, fossil-based polymers, and biopolymers that are produced by microalgae and cyanobacteria.

| Polymer | Crystallinity (%) | Elongation at Break (%) | Tensile Strength (MPa) | Melting Point (°C) | Glass Transition Temperature (°C) | References |
|---|---|---|---|---|---|---|
| PP | 60 | 400 | 38 | 176 | −10 | Balaji *et al.* (2013); Hazer and Steinbüchel (2007); Verlinden *et al.* (2007) |
| HDPE | 70 | 12 | — | 129 | — | Costa *et al.* (2019) |
| PHB | 57 | 6.2 | 31 | 173 | 1.6 | Balaji *et al.* (2013); Verlinden *et al.* (2007); Koller and Rodríguez-Contreras (2015); Garcia-Garcia *et al.* (2016); Simonazzi *et al.* (2021); Bhati and Mallick (2012) |
| PHBV | 53 | 70 | 23 | 153 | −2.9 | Balaji *et al.* (2013); Hazer and Steinbüchel (2007); Verlinden *et al.* (2007); Bhati and Mallick (2012); Samantaray and Mallick (2014) |
| PHB/PCL (75/25) | 58 | 11 | 21 | 169 | — | Garcia-Garcia *et al.* (2017) |
| PHB/PCL (25/75) | — | 125 | 11 | 154 | — | Przybysz *et al.* (2018) |

*Source:* Adapted from Mastropetros *et al.* (2022).
PP, polypropylene; HDPE, high-density polyethylene; PHB, polyhydroxybutyrate; PHBV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PCL: polycaprolactone. —, not reported.

with similar thermal and mechanical properties to petroleum-based plastics (Bhatia *et al.*, 2021; Medeiros Garcia Alcântara *et al.*, 2020). The first reported microbial production of PHAs dates back to 1926, from the bacterium *Bacillus megaterium* (Możejko-Ciesielska & Kiewisz, 2016). Even though bacteria have been reported to accumulate up to 90% of cell dry mass in PHAs (Obruča *et al.*, 2022), the high demand for organic carbon results in increased costs that pose a challenge in its widespread application. Microalgae and cyanobacteria can be promising alternative ways to produce PHAs. As photosynthetic microorganisms, they can utilize solar energy and $CO_2$ for their biomass growth while they have low-nutrient requirements (Costa *et al.*, 2019).

### 11.3.1 Cultivation conditions

Around 100 strains of microalgae and cyanobacteria have been reported to produce PHAs during their growth. Microalgae and cyanobacteria naturally accumulate these biopolymers as a source of carbon and energy. However, the production of PHAs is a complex metabolic process. The biomass productivity as well as the percentage and the type of PHAs that are produced depend on various parameters such as the selected carbon source and the availability of nutrients and light (Bagatella *et al.*, 2022; Cassuriaga *et al.*, 2018).

#### *11.3.1.1 Photoautotrophic, heterotrophic, or mixotrophic operational mode*

In response to shifting environmental conditions, microalgae and cyanobacteria employ different metabolic pathways. In cyanobacteria and microalgae, there are three delineated growth mechanisms. During photoautotrophic metabolism, the cells use $CO_2$ as a source of carbon and light as a source of energy. Under heterotrophic growth, microalgae and cyanobacteria meet their carbon and energy needs by consuming organic substances. Mixotrophic conditions combine both photoautotrophic and heterotrophic metabolic functions: energy and carbon needs can be covered by light or organic substances and organic or inorganic carbon sources, respectively. The significance of the different metabolic pathways in the cultivation of microalgae lies in their impact on the substrate that is being utilized, the amount of biomass produced, the growth rate, and the macromolecular composition of the cells.

Table 11.2 summarizes PHA production from microalgae and cyanobacteria during their growth by employing natural metabolic pathways. Photoautotrophic microalgae and cyanobacteria can accumulate PHAs (Phalanisong *et al.*, 2021). Apart from the production of these valuable compounds, these photosynthetic microorganisms can capture and utilize atmospheric $CO_2$ which contributes to carbon fixation (Phalanisong *et al.*, 2021). It has been reported that *Chlorella vulgaris*, *Scenedesmus obliquus*, and *Spirulina* sp. can remove $CO_2$ with efficiencies of 80, 28, and 53%, respectively (de Morais & Costa, 2007; Sadeghizadeh *et al.*, 2017). Few studies have reported the production of PHAs from eukaryotic microalgae in a photoautotrophic environment. More specifically, during their cultivation, *Botryococcus braunii*, *Chlorella pyrenoidosa*, and *Chlorella fusca* accumulated PHB at a concentration of 16, 27, and 5.5%, respectively (Cassuriaga *et al.*, 2018; Das *et al.*, 2018; Kavitha *et al.*, 2016b). Unlike microalgae, substantial amounts of PHAs are found in many cyanobacteria grown photoautotrophically. Several cyanobacterial strains such as *Nostoc*, *Synechocystis*, *Synechococcus*, and *Spirulina* naturally synthesize PHB at a content lower than 10% (Sirohi *et al.*, 2021).

Perceptibly, the addition of organic substances (e.g., acetic acid, xylose, glucose, and sucrose) increases the yields of PHB in cyanobacteria and microalgae (Price *et al.*, 2020). With the addition

**Table 11.2** PHA production from microalgae and cyanobacteria during their cultivation under photoautotrophic, heterotrophic, or mixotrophic conditions.

| Microbial Species | Mineral Medium | Carbon Source | Condition | Type of PHA | PHA Content (%) | References |
|---|---|---|---|---|---|---|
| *B. braunii* | CHU-13 | — | p | PHB | 16 | Kavitha *et al.* (2016b) |
| *S. salina* | BG-11 | — | p | P(3HB) | 6.6 | Kovalcik *et al.* (2017) |
| *C. pyrenoidosa* | Fogg's | — | p | PHB | 27 | Das *et al.* (2018) |
| *Spirulina* sp. | Zarrouk | — | p | PHB | 21 | Martins *et al.* (2017) |
| *Nostoc ellipsosporum* | BG-11 | — | p | PHB | 19 | Martins *et al.* (2017) |
| *C. fusca* | BG-11 | — | p | PHB | 0.5–5.5 | Cassuriaga *et al.* (2018) |
| *N. muscorum* | BG-11 | — | p | PHB | 8.5 | Sharma and Mallick (2005) |
| *N. muscorum* | $NO_3$-free BG-11 | 0.11% acetate + 0.08% propionate | m | PHBV | 31 | Mallick *et al.* (2007) |
| *C. fusca* | BG-11 | 0.002% xylose | m | PHB | 17 | Cassuriaga *et al.* (2018) |
| *Aulosira fertilissima* | BG-11 | 1% fructose | m | PHB | 16 | Samantaray and Mallick (2012) |
| *A. fertilissima* | BG-11 | 0.3% acetate | m | PHB | 27 | Samantaray and Mallick (2012) |
| *Synechocystis* sp. | BG-11 | 0.4% fructose + 0.4% acetate | h | PHB | 38 | Panda and Mallick (2007) |
| *Chlorogloeopsis fritschii* | BG-11 | 0.06% acetate | m | P(3HB) | 15 | Zhang and Bryant (2015) |

p, photoautotrophic; m, mixotrophic; h, heterotrophic.—, not reported.

of 20 mg/L xylose, the PHB content in *C. fusca* LEB 111 increased to 17% from the 5.3% that was observed in the photoautotrophic culture under the same conditions (Cassuriaga *et al.*, 2018). A significant increase was observed in the PHB content of *Nostoc muscorum* by adding different sources of organic carbon (Sharma & Mallick, 2005).

#### 11.3.1.2 Nutrient availability

Nitrogen is a key component of proteins, nucleic acids, and chlorophyll which are necessary for the structure and function of cells (Zarrinmehr *et al.*, 2020), and therefore is an important macronutrient that affects growth. In microalgae and cyanobacteria cultivation, the availability of nitrogen must be carefully monitored to achieve optimal growth and productivity. Nitrogen can be obtained from various sources including inorganic nitrogen compounds such as nitrate, nitrite, and ammonium, and organic compounds such as urea. Nitrate is the most commonly used source of nitrogen in microalgae (Yaakob *et al.*, 2021).

Phosphorus is another important macronutrient, where nucleic acids, cell membranes, and energy storage molecules such as adenosine triphosphate are among the many cellular structures that depend on it. To promote their growth, microalgae and cyanobacteria can absorb phosphorus in the form of polyphosphate or orthophosphate, with preference for the latter due to easier assimilation (Yaakob *et al.*, 2021).

Table 11.3 presents the PHA content from different microalgae and cyanobacteria strains during their cultivation under nitrogen and phosphorus deficiency. Nitrogen and phosphorus limitation affect both biomass growth and productivity. When these nutrients are limited, the cells redirect the excess carbon toward the biosynthesis of storage compounds such as PHAs, which can be used as an energy and carbon sources under adverse conditions (Costa *et al.*, 2019). Several studies have shown an increase in PHA content in many species under nitrogen and phosphorus starvation, regardless of the cultivation mode (photoautotrophic, heterotrophic, or mixotrophic) (Dang *et al.*, 2022; Troschl *et al.*, 2017; Yashavanth *et al.*, 2021). Kaewbai-Ngam *et al.* (2016) tested 137 cyanobacterial strains for their ability to accumulate PHB. Under nitrogen limitation conditions, PHB yield increased more than 50% of

**Table 11.3** PHA production from microalgae and cyanobacteria under nutrient limitation.

| Species | Culture Conditions | Nutrient Limitation | Type of PHA | PHA Content (%) | References |
|---|---|---|---|---|---|
| *Synechocystis* sp. | Photoautotrophic | N-deficiency, P-deficiency | PHB | 16 | Kamravamanesh *et al.* (2017) |
| *N. muscorum* | 0.28% acetate, 0.38% glucose, 0.30% valerate | N-deficiency | PHBV | 78 | Bhati and Mallick (2015) |
| *Scenedesmus* sp. | Glucose | P-deficiency | PHB | 30 | García *et al.* (2021) |
| *Synechococcus* sp. | Photoautotrophic | P-deficiency | PHB | 55 | Nishioka *et al.* (2001) |
| *N. muscorum* | Photoautotrophic | N-deficiency, P-deficiency | PHB | 23 | Panda *et al.* (2005) |
| *N. muscorum* | 0.20% acetate | N-deficiency, P-deficiency | PHB | 35 | Sharma and Mallick (2005) |
| *A. fertilissima* | 0.50% acetate | P-deficiency | PHB | 77 | Samantaray and Mallick (2012) |
| *Spirulina platensis* | 0.50% sodium acetate | N-deficiency | P(3HB) | 10 | Toh *et al.* (2008) |
| *A. fertilissima* | 0.26% citrate, 0.28% acetate | P-deficiency | PHB | 85 | Samantaray and Mallick (2012) |

the screened cyanobacterial strains. *Synechococcus* sp., a thermophilic cyanobacterium, accumulated 55% PHB when it was grown photoautotrophically and under phosphate limitation (Nishioka *et al.*, 2001). The PHB content in *N. muscorum* grown photoautotrophically and heterotrophically (0.2% acetate) achieved 22.7 and 35% under nitrogen and phosphate deficiency, respectively (Panda *et al.*, 2005; Sharma & Mallick, 2005).

#### *11.3.1.3 Light*

The growth of microalgae and cyanobacteria is in most cases significantly affected by light. Under photoautotrophic and mixotrophic conditions, light is essential for photosynthesis, which produces the required energy for cell growth. Under low-light intensities, the growth of microalgae and cyanobacteria can be limited due to limited photosynthetic activity. Excessively high-light intensities can also have negative effects such as photoinhibition and cell damage. Consequently, the intensity and availability of light affect biomass production as well as the accumulation of valuable compounds such as PHAs. However, the optimal light intensity and periodicity vary based on several factors, including the selected strain and the turbidity of the cultivation medium.

Several studies have investigated the impact of light intensity and alternation of light-to-dark cycles on the productivity of PHAs by microalgae and cyanobacteria (Costa *et al.*, 2019; Price *et al.*, 2020). In the study of Ansari and Fatma (2016), *N. muscorum* was cultivated at a light intensity of 25 $\mu$mol/m$^2$/s under three different photoperiods. At 0.4% glucose and in 14:10, 12:12, and 10:14 h light/dark periods, its PHB content was 18, 21, and 24%, respectively. In another study, the PHB content in *C. fusca* increased from 5.3 to 17.4% when light intensity decreased from 58 to 28 $\mu$mol/m$^2$/s under a 6:18 h light/dark period, whereas at the same light intensities, the PHB content was 5.5 and 2.7% under a 12:12 h light/dark period (Cassuriaga *et al.*, 2018). Optimizing the light intensity and photoperiod based on the specific strain being cultivated and culture conditions can be an effective strategy to enhance PHA production.

#### *11.3.1.4 Wastewater as a feedstock for microalgae and cyanobacteria cultivation*

Wastewater instead of a potential environmental hazard can be seen as a potential source of nitrogen and phosphorus for the growth of microalgae and cyanobacteria and be upgraded to valuable products (Sakarika *et al.*, 2022). The cultivation of these photosynthetic microorganisms in wastewater is a promising alternative to wastewater treatment as high nutrient removal and high biomass productivity can be achieved (Rizwan *et al.*, 2018). Cultivation of *S. obliquus* in soybean wastewater removed 72% of chemical oxygen demand, 95% total nitrogen, and 54% total phosphorus (Shen *et al.*, 2020). Similarly, *C. vulgaris* cultivated in meat wastewater removed 89% of chemical oxygen demand, 52% of total nitrogen, and 70% of total phosphorus (Hu *et al.*, 2019).

The cost of PHA production from microalgae and cyanobacteria is high compared to the conventional plastics industry. High feedstock and water requirements account for more than 50% of the production cost (Medeiros Garcia Alcântara *et al.*, 2020). To enable cost-effectiveness and feasibility on a larger scale, scientific interest has focused on the utilization of wastewater as a substrate for the cultivation of microalgae and cyanobacteria. Apart from the reduction of the upstream cost of the process and the bioremediation of wastewater, using wastewater as feedstock does not compete with raw materials such as sugars, which can also be used for PHA production (Medeiros Garcia Alcântara *et al.*, 2020). Studies have demonstrated that during the cultivation of microalgae and cyanobacteria in wastewater it is feasible to produce substantial amounts of PHAs with similar properties to conventional plastics. A PHB yield of 247 mg/L was reported by *B. braunii* grown in sewage wastewater at a concentration of 60% (Kavitha *et al.*, 2016a). In another study, *Synechocystis* sp. grown on shrimp wastewater accumulated PHB at a concentration of 33% while the removal efficiency of phosphate was 97% (Krasaesueb *et al.*, 2019).

Table 11.4 summarizes the production of PHAs from microalgae and cyanobacteria cultivated in different types of wastewater. Among the different wastewater types, anaerobic digestion effluents are

**Table 11.4** PHA production from microalgae and cyanobacteria cultivated in wastewater.

| Species | Type of Wastewater | Temperature (°C) | pH | Type of PHA | PHA Content (%) | References |
|---|---|---|---|---|---|---|
| *Synechocystis* sp. | Shrimp wastewater | 27–30 | 7.0–9.0 | PHB | 34 | Krasaesueb *et al.* (2019) |
| *N. muscorum* | Poultry litter | $25 \pm 2$ | 7.0 | PHB | 23 | Bhati and Mallick (2016) |
| *N. muscorum* | Poultry litter + 10% $CO_2$ | $25 \pm 2$ | 7.0–8.0 | PHBV | 65 | Bhati and Mallick (2016) |
| *S. salina* | Digestate supernatant | $25 \pm 1$ | — | PHB | 6.3 | Meixner *et al.* (2016) |
| *Synechocystis* sp. | 30% palm oil mill effluent + BG-11 medium | 28 | 8.2 | PHB | 15 | Nur *et al.* (2023) |
| *Synechococcus* sp. | 30% palm oil mill effluent + BG-11 medium | 28 | 8.2 | PHB | 15 | Nur *et al.* (2023) |
| *B. braunii* | 50% palm oil mill effluent + glycerol + Fe-EDTA* | 30 | 7.5 | PHB | 33 | Nur (2022) |

*EDTA, ethylenediaminetetraacetic acid; —, not reported.

generated in high volumes urging the need to implement a more sustainable disposal way than the current use as fertilizer. Digestates can be upgraded to higher value products when used as a substrate for the cultivation of microalgae and cyanobacteria and the production of value-added compounds as they contain high organic matter and are rich in nutrients such as ammonium-nitrogen and phosphorus (Kaur *et al.*, 2020; Koutra *et al.*, 2018). Only a few studies have investigated the production of PHAs from microalgae and cyanobacteria in digestates. For instance, *Synechocystis salina* was cultivated in diluted digestate and accumulated PHB at a concentration of 6.3% (Meixner *et al.*, 2016).

Overall, the cultivation of microalgae and cyanobacteria in wastewater seems to be an environmentally friendly and promising alternative for sustainable wastewater treatment and production of PHAs. However, fluctuations in the composition of the produced wastewater and the presence of potentially hazardous components can affect the entire process and even inhibit the growth of microalgae and cyanobacteria. Further studies to address these challenges are necessary before the implementation of the process at a larger scale (Mastropetros *et al.*, 2022; Medeiros Garcia Alcântara *et al.*, 2020).

### 11.3.2 Advantages of PHA production from microalgae and cyanobacteria compared to bacteria

PHAs are naturally produced by various microorganisms, with bacteria in the genera *Pseudomonas*, *Ralstonia*, *Bacillus*, and *Aeromonas* accumulating PHAs at high content. However, PHA production using bacteria is expensive and not feasible for large-scale applications due to the prohibitive cost of the organic carbon sources and oxygen requirements (Możejko-Ciesielska & Kiewisz, 2016; Samantaray & Mallick, 2015).

On the contrary, microalgae and cyanobacteria seem to be promising microorganisms for PHA production, utilizing atmospheric $CO_2$ and generating energy through photosynthesis. These photosynthetic microorganisms do not need exogenous organic sources for their biomass growth reducing the overall cost of the process by up to 50% (Medeiros Garcia Alcântara *et al.*, 2020; Phalanisong *et al.*, 2021). Microalgae and cyanobacteria can utilize $CO_2$ that is present in flue gases for PHA production, providing a sustainable solution to greenhouse gas emissions and making the process economically feasible. For instance, *S. salina* and *Synechococcus elongatus* directly utilizing industrial flue gases accumulated PHB at a content of 6.6 and 11%, respectively (Roh *et al*., 2021; Troschl *et al*., 2017).

Moreover, microalgae and cyanobacteria can produce more than one bioproduct. For instance, they can accumulate high amounts of lipids, proteins, polyunsaturated fatty acids, and pigments that can be utilized as raw materials for producing bioenergy and other valuable products used in a variety of sectors including food, cosmetics, nutraceutical, and pharmaceutical industries (Kumar *et al*., 2020). The implementation of a biorefinery concept is a complex procedure, where both upstream and downstream processing can significantly affect the entire process. The type and yield of the produced compounds strongly depend on the selected strains and the cultivation conditions while developing effective methods for extracting and purifying the various compounds from the microbial biomass is challenging and requires a considerable amount of energy (Siddiki *et al*., 2022). There are only a few experimental data available for the simultaneous production of PHAs and other valuable compounds in a biorefinery concept. *Arthrospira platensis* cultivated in palm oil mill effluent was investigated for the co-production of PHB and C-phycocyanin. Results showed that the productivities of PHB and C-phycocyanin using 50% palm oil mill effluent were 7 and 16 mg/L/day, respectively (Nur, 2022). Another study demonstrated the possibility of cultivating *Synechocystis* sp. in secondary effluent to produce PHB and lipids (Senatore *et al*., 2023). The ability of microalgae and cyanobacteria to utilize flue gases and wastewater to produce PHAs as well as other valuable compounds in a biorefinery concept can render the microalgae cultivation technology at a large scale economically feasible and environmentally friendly.

### 11.3.3 PHA blends

PHAs present several environmental benefits as bio-based and biodegradable polymers. However, their industrial application is still limited due to their high production cost. Additionally, for PHA production to become competitive with the petroleum-based plastic industry, the produced biopolymer must have similar properties to conventional plastics. To overcome these limitations, blending PHAs with raw materials and other biodegradable polymers has emerged as a promising and simple approach. The type and properties of the produced polymer blends depend on the choice of the starting constituents and their blending ratio. PHA blending aims to improve the mechanical properties, such as increased tensile strength, elongation at break, and impact resistance, that can be used in a wide range of applications, enhance the biodegradability of the material, reduce the cost, and improve the overall performance (Kumar *et al*., 2021).

#### *11.3.3.1 PHA blends with raw materials*

Starch is considered a highly promising natural polymer because it is biodegradable and widely available in large quantities. PHA/starch blends have improved mechanical properties compared to pure PHAs. In the study of Asl *et al*. (2021), an electrospinning method was used to blend PHB with different concentrations of starch (5–15 wt%). By adding starch at a concentration of up to 10%, the tensile strength of the PHB/starch scaffolds increased from 3 to 16 MPa. The presence of starch also enhanced the thermal stability and degradation rate. The results of this study suggest that electrospun scaffolds produced from PHB/starch could be used in bone tissue engineering applications. In another study, the blend of PHB with modified corn starch was investigated. When the starch concentration increased, an increase in glass transition temperature from 2 to 37°C was observed (Lai *et al*., 2015). The mechanical and thermal properties of PHA/starch blends can be significantly improved with the addition of cross-linking agents such as citric and adipic acids (Sun *et al*., 2018).

Lignin is a complex organic polymer and the second most abundant renewable natural polymer on the Earth. PHA blends with lignin offer a promising approach to the development of new materials with improved mechanical properties and biodegradability compared to either material alone. Therefore, by combining lignin with PHAs, it is possible to create new materials with a range of desirable properties that can be used in various applications (Kumar *et al*., 2021). Lugoloobi *et al*. (2020) reported that

PHB/lignin blends showed higher glass transition temperatures, improved ultraviolet resistance and tensile performance, and higher melt viscosity making them suitable for packaging applications.

Cellulose derivatives are becoming increasingly popular as components that can be blended with PHAs due to their compatibility and their ability to accelerate the degradation of PHAs. Cellulose, acetate, butyrate, ethyl cellulose, and cellulose propionate are cellulose derivatives that are commonly used as drug carriers, blood coagulants, and coatings for pharmaceutical tablets (Sharma *et al*., 2021). Cellulose-based microfibers (MFs) can be used to enhance the properties of PHA films. According to Mármol *et al*. (2020), the addition of MFs made the PHA film 23% more durable, as both the tensile strength and Young's modulus increased. Overall, PHA blends with raw materials result in new biopolymers with improved properties when compared to either of the individual components.

#### *11.3.3.2 PHA blends with biodegradable polymers*

PLA is a biodegradable polymer derived from renewable resources. Blending PHAs with PLA is the most studied approach as it can result in material with improved mechanical properties and biodegradability, with the specific properties depending on the PHA to PLA ratio. The PHA/PLA blend has been used in three-dimensional printing, where the printed materials exhibited favorable mechanical properties and thermal stability (Ausejo *et al*., 2018). In another study, the PHA/PLA blend was demonstrated to have the capacity to absorb oil from water, which is similar to that of currently utilized absorbents (Iordanskii *et al*., 2019).

Polycaprolactone (PCL) is a synthetic biodegradable polymer with a low melting point. Blending PCL with other biopolymers, such as PHAs, can improve biodegradability and decrease the production cost. The degradation rate of the blend as well as the mechanical properties can be controlled by adjusting the ratio of PCL to PHA. For instance, higher maximum stress was exhibited in blends rich in PHB, whereas blends rich in PCL led to greater strain at break. The PCL/PHA blend can be utilized in various biomedical applications, especially in tissue engineering (Kumar *et al*., 2021; Li *et al*., 2016).

Blending PHAs with poly(butylene adipate-*co*-terephthalate) (PBAT) is another approach to developing biodegradable polymer blends with improved properties and increasing the field of their application (Tian & Wang, 2020). Similar to PCL, PBAT is a synthetic biodegradable polymer. The blend can be processed using common techniques such as injection molding and extrusion. During injection molding of PHBV with PBAT, as the PBAT content increased the toughness and strain at break increased, while the specific modulus and strength decreased (Javadi *et al*., 2010). In another study, the addition of PBAT increased the shear storage modules of the PHB/PBAT blends and decreased the tensile storage modulus (Larsson *et al*., 2016). Overall, blending PHAs with other biodegradable polymers is a promising alternative to reduce production costs and develop new materials with improved properties and biodegradability, making them attractive for a wide range of applications.

## 11.4 DOWNSTREAM PROCESSING OF BIOPLASTIC RECOVERY FROM MICROALGAE AND CYANOBACTERIA

During the past few years, increased research efforts aim at developing more efficient harvesting, pretreatment, and extraction techniques, with the hope of lowering the cost of microalgal bioplastics production. These efforts include exploring and evaluating various methods and technologies that can be used to optimize the downstream process. By reducing the costs associated with these production stages, the development of sustainable bioplastics derived from microalgae and cyanobacteria can become economically viable and contribute to a more sustainable future. In addition, this can also lead to the development of new and more efficient approaches to produce other valuable products from these microorganisms toward a biorefinery concept.

### 11.4.1 Harvesting

The relatively low final biomass concentrations in microalgal and cyanobacterial cultures (with values from 0.5 g/L in open-pond systems to 5 g/L in photobioreactors), resulting from light restriction due to shading from cell growth, lead to the urge for separation of the biomass from a large water volume (Pahl *et al.*, 2013; Vandamme *et al.*, 2013). To achieve the desired solid–liquid separation during harvesting, various mechanical-, chemical-, biological-, or electrical-based techniques can be used through one or more steps (Mata *et al.*, 2010; Morais Junior *et al.*, 2020). The selection of an appropriate harvesting method depends on several factors, such as the microalgal cell morphology (e.g., filamentous, spherical, or elongated), the biomass concentration in the culture medium, the specific gravity, and size (typically microalgae will be in the range of 0.5–200 μm) of cells (Caroppo & Pagliara, 2022; Gerardo *et al.*, 2015; Roy & Mohanty, 2019). Additionally, the surface charge of microalgae and cyanobacteria, which is estimated by their zeta potential, plays a key role in downstream processing by preventing cells from clumping together and leading to a stable cell suspension (Krishnan *et al.*, 2022). This potential can fluctuate significantly, depending on factors such as cell age and culture conditions (e.g., salinity and pH), and ranges from −5 to −80 mV (Greenwell *et al.*, 2010; Yang *et al.*, 2022; Zhang *et al.*, 2013). Considering the above, harvesting biomass is one of the main obstacles in downstream processing as it requires large amounts of energy and it has been stated that the cost of collecting and drying the biomass from wet cultures is ∼20–30% of the total operational cost of biomass production (Molina Grima *et al.*, 2003; Price *et al.*, 2022).

Highly efficient and minimally damaging methods for separating the biomass from the culture medium are essential during harvesting. There is a plethora of available methods for harvesting microalgae and cyanobacteria (Vasistha *et al.*, 2021), where the appropriate method depends on the characteristics of the microorganism, the properties of the culture medium, and the intended application of the harvested biomass. Furthermore, it is a widespread practice to combine two or more methods to achieve a higher separation efficiency while reducing the costs involved (Barros *et al.*, 2015). Next, we discuss various separation techniques for microalgal and cyanobacterial biomass harvesting.

#### *11.4.1.1 Centrifugation*

Centrifugation methods use force to separate particles based on the different densities between the particles. This allows microbial cells, that are denser than the culture medium, to settle (Pahl *et al.*, 2013). Centrifugation is one of the most common harvesting methods on lab scale and can be applied to most microalgae and cyanobacteria. Compared to gravity sedimentation, centrifugal force accelerates sedimentation, leading to a higher biomass recovery efficiency. Additionally, centrifugation eliminates the need for chemicals (e.g., flocculants), which could decrease the quality of the biomass. However, the high energy requirements (up to 8 kWh/$m^3$) limit its large-scale application to high-value products (Barros *et al.*, 2015; Laamanen *et al.*, 2016; Pahl *et al.*, 2013).

#### *11.4.1.2 Filtration*

Membrane filtration is a commonly used technique for biomass separation and can be considered a viable harvesting option. During this process, the liquid fraction of the culture is allowed to pass through a porous membrane, usually by applying pressure or a vacuum to the system, while the cells are retained. The ability of solute or solid to pass through a particular porous membrane is dependent on its dimensions, electrical charge, and morphology. Additionally, factors such as the viscosity and mixing rate of the suspension can impact this process (Mathimani & Mallick, 2018). Due to the relatively low-energy requirements (0.2–0.88 kWh/$m^3$) and cost, combined with the ease of scalability, this method is highly advantageous (Pahl *et al.*, 2013). Also, similar to centrifugation, no chemicals are needed, thereby avoiding the qualitative degradation of the recovered biomass. However, the accumulation of microalgal deposits on the filter, leading to fouling (or clogging) of the membrane is the primary limitation of these methods, and it raises their operational costs. Membrane fouling is primarily caused by extracellular polymeric substances (EPSs), which are organic compounds secreted by microalgae during their growth or released upon cell lysis (Singh & Patidar, 2018).

#### 11.4.1.3 Flocculation and coagulation

Flocculation/coagulation is an economical method for harvesting microalgae and cyanobacterial biomass due to large culture volumes and the need for a universal process that can be applied to various species. Flocculation/coagulation involves the use of inorganic (e.g., $Al_2(SO_4)_3$, $FeCl_3$, and $Fe_2(SO_4)_3$) or organic (e.g., poly(diallyldimethylammonium chloride), PDADMAC) salts, which work by neutralizing the negative charges of cells, resulting in clustering of particles, allowing the suspension to concentrate up to 100 times (Mubarak *et al.*, 2019; Singh & Patidar, 2018; Vandamme *et al.*, 2013). Combining this technique with gravity sedimentation reduces the energy demand of the overall operation, leading to an economically viable harvesting process (Barros *et al.*, 2015). However, a major disadvantage of using aluminum or iron salts as flocculants is that any remaining chemicals can be a potential environmental and health hazard. Also, the use of organic flocculants appears to negatively affect the levels of unsaturated fatty acids in the recovered biomass (Laamanen *et al.*, 2016). In recent years, several studies have been conducted on bioflocculation, in which microalgae cluster together with various microorganisms, including bacteria, fungi, or other microalgae (Kumar *et al.*, 2023). The above procedure can be carried out with the use of bioflocculants, which are usually EPSs produced by several microorganisms (Moreira *et al.*, 2022).

#### 11.4.1.4 Gravity sedimentation

One of the simplest methods for liquid–solid separation is gravity sedimentation. Although this form requires low operating and designing costs, the fluctuating densities and consequently the low sedimentation rates (0.1–2.6 cm/h) of most microalgae, make the process relatively time-consuming, with the risk of degrading the collected biomass (Barros *et al.*, 2015; Greenwell *et al.*, 2010). Therefore, in most cases, gravity sedimentation takes place after a flocculation/coagulation step (Chatsungnoen & Chisti, 2016). Finally, the high self-sedimentation property of some species, such as cyanobacteria *Chlorogloea fritschii*, *Phormidium* sp., and microalga *Golenkinia* sp., eliminates the need for additional energy and reduces the cost and time required to harvest biomass (Hotos *et al.*, 2023; Monshupanee *et al.*, 2016; Nie *et al.*, 2018).

#### 11.4.1.5 Flotation

Flotation is another separation technique based on air or gas bubbles that adhere to the surface of the particles, achieving their transport to the surface and facilitating the separation (Pahl *et al.*, 2013). Furthermore, some cyanobacteria float on their own, as they possess intracellular gas vesicles (aerotopes) (Duval *et al.*, 2021). Flotation is often combined with flocculation/coagulation techniques for optimal harvesting results. Flotation cells are typically supplied with air via dispersed air, dissolved air, or electrolytic mechanisms. Currently, the most common flotation methods are dissolved air flotation (with bubble diameters less than 100 μm), dispersed air flotation or foam flotation (bubble diameters between 100 and 1,000 μm), electrolytic flotation, and dispersed ozone flotation (Barros *et al.*, 2015). The efficiency of smaller sized gas bubbles increased, compared to larger bubbles, as they possess a larger surface area per unit volume. The larger the surface area, the greater is the chance of collision between air bubbles and particles (Pahl *et al.*, 2013). Qi *et al.* (2022) achieved a harvesting efficiency of 96% for the microalga *Tribonema* sp. using flotation, with a significantly lower amount of energy (0.19 kWh/kg biomass) compared to other harvesting methods.

### 11.4.2 Drying

The extraction techniques for most bioplastics (especially PHAs) from microalgae and cyanobacteria presupposes the drying of the biomass, as the residual water can have a significant effect on their efficiency. Thus, a reliable drying method such as freeze drying, convective drying, spray drying, or solar drying is necessary (Levett *et al.*, 2016). It is estimated that biomass drying can account for up to 20% of the overall cost of producing PHAs from cyanobacteria, posing a barrier to upscaling commercial production (Costa *et al.*, 2019). Solar drying is an inexpensive dehydration technique but requires extended drying periods, due to the low temperature, and a large land area. In addition, the slow dehydration rate can promote bacterial growth and consequently degradation of the microalgal biomass (Chen *et al.*, 2015). However, in closed solar systems an increase in the drying rate can be achieved, leading to drying of the biomass in 3–5 h at a temperature of 60°C (Prakash *et al.*, 1997). Lyophilization (freeze drying) and spray drying are techniques commonly used to remove water from microalgal biomass. Unlike convective drying, these methods preserve all cellular components without damaging the cell wall (Chen *et al.*, 2015). Spray drying is generally considered more advantageous than lyophilization due to its faster drying speed, ability for continuous operation, and lower cost, but there is a greater possibility of oxidation of carotenoids (Zhang *et al.*, 2022). Nevertheless, until now there is no evidence on how each drying method affects the structure and physicochemical characteristics of the recovered PHAs from microalgal/cyanobacterial biomass.

### 11.4.3 Extraction

Recent research efforts have focused on developing extraction techniques that reduce the overall cost of producing bioplastics. The commonly used extraction methods are based on organic solvents, usually halogenated. Chloroform and dichloromethane are commonly used solvents as they dissolve bioplastics but no other biological products (Levett *et al.*, 2016). After biomass dehydration, the disruption of the cell membrane takes place, which can be achieved using organic solvents or physical stress, so that the solvent can come into contact with the PHA granules, which are trapped intracellularly (Mastropetros *et al.*, 2022). Additionally, a pretreatment step could be applied prior to extraction to enhance the recovery, usually using sodium hypochlorite (Kosseva & Rusbandi, 2018). Following the extraction of bioplastics from the dry biomass, a suitable solvent such as methanol is used for the recovery, and partial purification of the product, a method known as liquid antisolvent precipitation. Although organic solvents are effective in creating a product with minimal reduction in the molecular weight of the polymer, they are costly and are an environmental hazard (Kosseva & Rusbandi, 2018). Therefore, new environmental-friendly, sustainable, and profitable technologies are needed to scale up and commercialize bioplastic production.

Biomass hydrolysis could be a potential method for recovering biopolymers. By using an acid or base solution, the cells are hydrolyzed, leaving the bioplastic granules undissolved (López-Abelairas *et al.*, 2015). However, some chemical compounds used for this process seem to have a negative effect on the molecular weight and characteristics of the recovered bioplastics (Mastropetros *et al.*, 2022). To prevent such issues, the use of enzymes (e.g., trypsin, bromelain and lysozyme) has been proposed, because they can denature the cell wall during biomass treatment without degrading PHAs. Enzymatic methods for PHA extraction typically involve a heat pretreatment and enzymatic hydrolysis (Kapritchkoff *et al.*, 2006).

Supercritical fluids, such as supercritical $CO_2$, have been suggested as substitutes for organic solvents for extracting and purifying PHAs. More specifically, supercritical $CO_2$ can extract up to 90% of the PHA content at purity levels ranging from 86 to 99% and can be used as a secondary step to remove oily biomass residues and refine the bioplastics (Kosseva & Rusbandi, 2018; Mastropetros *et al.*, 2022). However, the high operational costs associated with supercritical fluid extraction and purification processes have impeded their widespread implementation. Nevertheless, the non-hazardous, non-combustible, and low-reactivity nature of supercritical fluids makes them an attractive alternative to organic solvent extraction methods (Mastropetros *et al.*, 2022).

There are various biodegradable, eco-friendly, and recyclable solvents that can be used for the extraction and purification of PHAs, including alcohols, acetone, ketones, and ethylene carbonate. Dimethyl carbonate is another green solvent that shows good performance and does not cause degradation of PHAs such as halogenated solvents. Ethylene carbonate is also used to recover a higher quantity of PHAs without causing degradation (Kurian & Das, 2021). A recent study compared various solvents and found that dimethyl carbonate is a more environmentally friendly and less hazardous choice for PHA extraction from biomass (Koller, 2020). In addition, ionic liquids are being increasingly favored as a solvent for extraction, and they have the potential to replace traditional organic solvents, as they behave similarly because of their electrically charged ions (Mastropetros *et al*., 2022). It has been noted that the use of ionic liquids as solvents for extraction offers the benefit of being able to recover the ionic liquid, thereby increasing the viability of the process (Dubey *et al*., 2018).

## 11.5 CHALLENGES AND FUTURE PERSPECTIVES

One of the main bottlenecks in the widespread adoption of PHAs from microalgae and cyanobacteria is their accumulation at low percentages on a dry weight basis. Therefore, strategies to enhance the productivity of PHAs are necessary. Process optimization by controlling the cultivation conditions, such as light intensity, pH, and temperature can improve microalgal growth and PHA accumulation. Supplementation of organic carbon sources (e.g., simple sugars) and nutrient limitation (e.g., nitrogen or/and phosphorus starvation) have also been reported to increase PHA accumulation by microalgae and cyanobacteria (Costa *et al*., 2019). Strain improvement via genetic engineering could be another option to enhance the production of PHAs. For instance, genetic modification of *Synechocystis* sp. enhanced PHB production up to 35% in dry cell weight (Sirohi *et al*., 2021). However, there are concerns related to the safety and ethical implications of using genetically modified microorganisms (Chia *et al*., 2020; Sirohi *et al*., 2021).

The industrial application of PHA production is still limited due to its high cost. Despite the technological advances, PHA costs 5€/kg compared to the production cost of synthetic plastics, which ranges from 0.8€ to 1.5€/kg. One way to reduce the production cost is to reduce the cultivation cost. The feedstock used for the cultivation of microalgae and cyanobacteria represents more than half of the production cost. The utilization of wastewater streams as raw materials seems to be a promising alternative as they are widely available and enriched in organic carbon and nutrients that microalgae and cyanobacteria need for their growth and the production of valuable compounds. This approach will not only diminish the cost of PHA production but also contribute to the bioremediation of wastewaters. However, several issues need to be addressed. The feedstock composition strongly affects the type and yield of PHA produced. The combination of different streams of wastewater or their dilution with water can assure its constant characteristics and decrease the turbidity caused by suspended particles. Furthermore, cultivation in wastewater can affect the end-life of the produced PHA as it may contain impurities that could potentially compromise the biocompatibility of the resulting plastics (Khatami *et al*., 2021; Medeiros Garcia Alcântara *et al*., 2020). As discussed in Section 11.3.1.1, microalgae and cyanobacteria can photoautotrophically accumulate PHAs using $CO_2$ as the sole carbon source. The capture of flue gases, which are rich in $CO_2$, for PHA synthesis can reduce the production costs while promoting $CO_2$ mitigation and the reduction of greenhouse gases with several environmental benefits (Sirohi *et al*., 2021).

The downstream processing is also a critical and costly step in the production of PHAs from microalgae and cyanobacteria. The properties, purity, and yield of the produced PHAs, apart from the potential for specific microalgae to produce them, also depend on the extraction methods used. The most common strategy is the extraction of PHAs with organic solvents such as chloroform and acetone. However, this method creates waste and need extra costs. Therefore, it is necessary to investigate alternative extraction methods, such as enzymatic ones, and the use of different solvents that are recyclable to establish downstream processes that are both cost-effective and environmentally sustainable without affecting the efficiency of the process (Kurian & Das, 2021).

The implementation of a biorefinery concept is a sustainable and economically viable method for PHA production. Cultivation of microalgae and cyanobacteria using carbon flue gases and wastewater for the production of PHAs and other value-added compounds has several environmental and economic benefits. The downstream processing in this approach is still challenging as the separation of the various compounds is difficult and a high amount of energy is required. In conclusion, PHA production from microalgae has the potential to be a more sustainable and environmentally friendly alternative to petroleum-based plastics. However, several challenges need to be addressed to enable cost-effective and scalable PHA production technologies.

## 11.6 CONCLUSION

To enable a more sustainable future, the transition toward the utilization of biodegradable bioplastic materials derived from renewable sources is necessary. Microalgae and cyanobacteria are promising candidates for PHA production which can have similar thermal and mechanical properties to conventional plastics. Considering that the downstream processing significantly affects the yield and the properties of the produced PHAs, further research is required to optimize the extraction methods as well as to decrease the dependence on organic solvents. However, the industrial application of bioplastics is still limited due to their high cost. Ongoing research has focused on enhancing the PHA productivity and reducing the cost of the process. PHA production is possible during the cultivation of microalgae and cyanobacteria in various types of wastewaters and side-streams, which could increase the sustainability of the process. Valorization of wastewater and $CO_2$ from flue gases in the cultivation of microalgae and cyanobacteria to produce PHAs and other valuable co-products such as biofuels and pigments can be the key to the application of bioplastics on an industrial scale.

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