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Review on Algal biopolymer - A combat to petroleum based plastics

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Abstract

Biopolymers are polymeric biomolecules produced by living biota viz., microorganisms, plants, aquatic animals and cyanobacteria. Such produced polymers are biocompatible, non toxic, flexible, biodegradable and significantly constitute a potential alternative to petrochemical derived polymers. Microalgae emerged as excellent producers of polymers with improved properties where Cyanobacteria (bluegreen algae), green microalgae, red microalgae and brown-golden microalgae produce valuable biomolecules such as pigments, lipids and exopolysaccharides. This review focus on exploring the knowledge on algal cultures potentials in the synthesis of biopolymer which fight against the environmental issues by playing as a substitute for existing carbon based plastic.

1. Introduction

Plastics have changed the everyday life as its usage is increasing day by day. These plastics are polymeric substances with immense properties such as strong, durable, lightweight and corrosion resistant which enables their use to make a wide variety of products as they can be melted, molded, remelted and remolded.

Mostly all aspects of daily life involves the use of plastics, such as in transport, clothing, packaging materials, telecommunications etc,. There is also considerable potential for novel applications of these plastics that will bring possible benefits in the future (Thompson *et al.,* 2009).There are different types of plastics such as Polyethylene Terephthalate (PET), High Density Polyethylene (HDPE), PolyvinylChloride(PVC), Low Density Polyethylene(LDPE), Polypropylene(PP), Polystyrene (PS) and the Miscellaneous type of plastics are polycarbonate, polylactide, acrylic, acrylonitrile butadiene, nylon, styrene and fibreglass Though plastics satisfy enormous human needs currently they are causing harmful effects to the environment and human health because they are carbon based polymers and the majority of their feedstock is primarily petroleum derived compounds that are not very good for the environment. The need of an alternative to existing plastic is necessary to solve the toxicity effects in the eco system.

1. Polymers:

Polymers are large molecules composed of long chains or rings of repeating subunits called monomers. Polymers possess high boiling and melting points. As they consist of many monomer units they tend to have high molecular masses (Anne Marie, 2019). They have unique properties depending on the type of bonding molecules. Some

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can bend and stretch like polyester and rubber while others are tough, hard and unstretchable like epoxies and glass (Ellis and Smith 2008). They may be natural or synthetic. Polymers result from chemical reaction of monomers. These monomers have the ability to react with same or different types of molecules to form a polymer chain under suitable condition. This resulted in the formation of natural polymers such as starch, cellulose and natural rubber, while synthetic polymers are made artificially by man (Namazi, 2017).

1.2 Structure of polymer:

Polymers are usually formed through polymerization process in which the repeated monomer molecules bond together by a chemical reaction which often results in a three dimensional network of polymer chains. There are two types of polymerization reactions - addition and condensation reactions.

Addition polymerization involves the formation of polymers from carbon - carbon double bonds containing monomers by exothermic addition process. The polymers often produced through this process include polyethylene, polyvinyl chloride, polypropylene, polystyrene etc., whereas in condensation reaction polymers are formed by a stepwise reaction of molecules having different functional groups. The reaction is endothermic and the polymers include polyesters, polycarbonate and polyamides. The properties of polymers depends on the varying functional groups within the molecular structure. The individual polymer chains entangle within each other which rely on forces such as hydrogen bonding, vanderwaals forces, dipole interactions but not the covalent bonds (Jansen, 2016).

1.3 Natural polymers:

Natural polymers are substances which are naturally obtained. Some of the natural polymers include chitin, cellulose, resins, protein, starch, natural rubber (Benabid and Zouai, 2016).). These polymers are found in plants and animal sources. The main advantage of using natural polymers is that they have no adverse effect on the human or environment and are biodegradable and non toxic compared to synthetic polymers. They are economically cheaper and low production cost than synthetic polymers (Kusum Kaushik *et al*.,2016).

1.4 Semi - synthetic polymers:

They are obtained by simple chemical treatment of naturally occurring polymers in order to change their physical properties. Some examples of semi synthetic polymers are silicones and starch (Kusum Kaushik *et al*.,2016).

1.5 Synthetic polymers:

These types of polymers are synthesized by polymerization of simple chemical molecules in the laboratory. They are human made plastics. Synthetic polymers are mostly petroleum based plastics. Some of the common synthetic plastics made are polyethene, polystyrene, PVC, Teflon, Synthetic rubber, Nylon etc., (Kusum Kaushik *et al*.,2016).They are mostly manufactured from hydrocarbons that are derived from crude oil. They have desirable properties such as strength, chemical flexibility, resistivity etc., (John Brennan,2017). The major drawback of synthetic polymer is their nondegradability and also synthetic plastics or polymers results in environmental issues because of improper disposal and brings threat to human health as they emit toxic fumes when burnt. The environmental pollution and exhaust of natural resources occurred because of these petroleum based synthetic polymers or plastics urged the need of environmentally benign polymers (Gowthaman *et al.*, 2021).

2. Biopolymers:

Biopolymers are polymeric biomolecules that are derived or extracted from the widely available resources such as microorganisms, marine animals and plants. These polymers are produced by these biological resources as biomass or byproduct during their growth cycles (Mukund Adsul *et al.*,2016).The prefix "bio" denotes that they are biodegradable. The materials that are produced by synthetic chemistry from biological sources such as sugars, resins, proteins, fats, vegetable oils etc., can also be described using the term biopolymers. The important property that distinguishes biopolymers from fossil fuel derived polymers is that their sustainability and especially their biodegradability. Hence these biodegradable biopolymers have been synthesized from renewable sources as an alternative for petroleum based plastics. They are usually synthesized from starch, natural fibers, sugars etc., and are easily degraded by microorganisms (Mohan *et al*., 2016).

2.1 Biopolymers from various sources:

2.1.1 Microbial Biopolymers:

Many microorganisms are known to produce biopolymers that are either found attached to the cell surface or separated from the fermentation medium. Biopolymers are a class of storage polymers produced by many microorganisms such as Bacteria, fungi etc.,(John Masani Nduko *et al.*,2019). There are four types of microbial polyesters such as cellulose based, starch based, lactic acid based and Polyhydroxyalkanoic acids (Lenz R.W *et al*.,2005). Among various microbial biopolymers PHA have been drawing attention due to their material properties and greater biodegradability. Hence PHA's are considered as a potent alternative for petrochemical plastics (Byrom, 1987). These PHA's are accumulated as granules in a variety of microorganisms intracellularly or extracellularly (Kunal *et al*.,2011).

3.7.1.1 Bacterial Biopolymers:

Bacteria are capable of synthesizing a variety of biopolymers with different biological functions and also with material properties. Bacteria converts different carbon sources into polymers with diverse chemical and material properties. Although bacteria only synthesize few intracellular polymers, the range of polymers that they can synthesize extracellularly is vast. Four classes of polymers are produced efficiently by bacteria such as : Polysaccharides, Polyamides, Polyesters, Polyanhydrides (Rehm, 2010).

Polysaccharides:

The polysaccharides produced by bacteria can be exopolysaccharides and endopolysaccharides. Glycogen is an endo or intracellular polysaccharides produced by many bacteria. Alginate is produced extracellularly by *Pseudomonas* and *Azotobacter* species. Xanthan is an exopolysaccharide produced by *Xanthomonas* spp. Cellulose is extracellularly synthesized by Alphaproteobacteria and many Gram positive bacteria

Polyamides:

Poly gamma glutamate is extracellularly produced by *Bacillus* sp, *Fusobacterium nucleatum* and few Gram positive bacteria.

Polyester:

Polyhydroxyalkanoate are energy reserve polymers belonging to polyester class of biopolymer produced by bacteria when the carbon source is high and other essential nutrients such as nitrogen, phosphorus, oxygen, sulfur are in limited amounts. PHA's are produced intracellularly by many bacterial species such as *Bacillus megaterium*, *Pseudomonas oleovorans*, *Azotobacter* etc., Among the PHA polymer family PHB

(Polyhydroxybutyrate) is the most common biopolymer accumulated under nutrient stress conditions and they act as energy storage material (Bernd Rehm,2010) (Hazer *et al.,* 2007)

Polyanhydrides:

Polyphosphate is a type of polyamide class of bacterial polymers produced intracellularly by many bacterial species such as *Spirillum volutans* (Bernd Rehm,2010) (Meyer A,1904).

2.1.2 Fungal biopolymers:

Fungi are also capable of effectively producing biopolymers. The cell wall of fungi is composed of polymers such as glucans and chitin (Araújo, 2020). Beta glucans are the type of biopolymer which consist of a backbone of glucose residues constitute half the mass of cell wall of fungi (Seviour *et al.,*1992) (Mclntosh *et al.* ,2005). Fungal species capable of producing glucans are *Saccharomyces cerevisiae, Peslatotia sp.,Epicoccum nigrum* etc.,(Gopal Rao *et al.,* 2014).

2.1.3 Algal Biopolymers:

Algae are one of the promising organisms for biopolymer production as grow fast and contain various value added materials and they have high bioenergy feedstock potential. Algae derived polymers are of three types - Natural polymers, Polyhydroxyalkanoate and Bio based polymer from algae derived monomer. They have similar characteristics as of conventional synthetic polymers (Didem Ozcimen *et al.,* 2017).

a) Algal Polysaccharides:

Marine algae are a rich source of polysaccharides such as cell wall structural polysaccharides, mucopolysaccharides and storage polysaccharides (Kim *et al.*,2015). The green algae contain a large amount of polysaccharides such as ulnas, xylan, sulfated galactans. Red algae are rich in Xylan, Carrageenan, Fucoidan, Porphyran (Murata *et al.*,2001) (Kumar *et al.*,2008). Brown algae are rich in alginic acid, laminarin, Sargassan and Fucoidan (Kim *et al.*,2015).

b) Alginate:

Alginate is a type of polysaccharides found in the cell wall of brown algae (Kim SK *et al.*,2015). The extraction method of alginate is that 100g of algae samples are ground and left overnight in 0.1M HCL and then washed in 1litre of 1% sodium carbonate solution which is then stirred and filtered. The filtrate obtained is collected and precipitated with isopropanal. The resulting gel is then dried and milled to *get al*ginate (Ozdemir *et al.*,2013).

c) Laminarin:

Laminarin is a storage polysaccharide of brown algae. It is a linear polysaccharide which constitute 25-50 glucose monomer units (Cybulska *et al.*, 2016). For extraction of laminarin, 85% of ethanol is applied at 23°c and 70°c in order to separate the proteins and other pigments from the algae which is then centrifuged. The pellet and solvent are separated by vacuum filtration with a filter paper. The pellet separated by filtration is then treated with 2% calcium chloride at 70°c and then centrifuged. The polymers alginate and Fucoidan and laminarin precipitates out. Fucoidin is then separated by treating with 0.01M HCL at 70°c and then centrifuged. The pellet is then subjected to 3% sodium carbonate to remove alginate from the solution and further centrifuged to obtain Laminarin (Ozdemir *et al.*,2013).

d) Fucoidan:

Fucoidan extraction is carried out in hot water. It is followed by precipitation with organic solvents. It involves 3 steps: milling, extraction/purification and drying (Kim SK *et al.*,2015).

e) Carrageenan:

It is a major constituent of red algae. For extraction of carrageenan, the algae is collected and dried. Then the dried sample is mechanically ground, sieved and washed. The cellulosic materials are removed by two stage treatment. First the dissolved carrageenan is centrifuged to remove cellulosic materials. It is then filtered to separate smaller particles. The solution is then concentrated by evaporation and the water content is removed. The carrageenan is then recovered by one of the two methods. The first method is to deposit carrageenan solution in potassium chloride. This allows the filtrate to gel which is then frozen and the excess water is removed by compression during the process of thawing. In the second method carrageenan solution is precipitated in Isopropyl alcohol. Since carrageenan is insoluble in alcohol it clots between alcohol and water. The clot is compacted to remove water content and then vacuum dried to remove alcohol content. The coagulum is then dried, milled and blended (Ozdemir *et al.*,2013).

f) **Agar:**

Agar is a mixture of polysaccharides which is composed of agarose and agaropectin. It has interchangeable structural and functional properties as that of carrageenan (Kim SK *et al.*,2015). Agar extraction involves the following step. The seaweed is washed and then boiled in water to dissolve the agar, it is then filtered and cooled to obtain jelly property and the water content is removed (Cybulska *et al.*,2016).

g) Ulvan:

It is a major constituent of green algal cell wall. It is composed of glucose, xylose, Iduronic acid, sulfate, rhamnose, glucuronic acid and smaller amounts of arabinose, mannose and galactose. It is of two kinds water soluble ulvan and insoluble cellulose like material (Kim *et al.*,2015).

2.1.4 Cyanobacteria:

Cyanobacteria are photosynthetic prokaryotes that capture sunlight as the source of energy using chlorophyll a and other accessory pigments. They are commonly found in lakes, ponds, streams, rivers, wetlands and they also play a significant role in nitrogen, carbon and oxygen dynamics of many aquatic environments. Cyanobacteria were classified as blue-green algae because of their appearance, possession of chlorophyll and photosynthetic production of oxygen similar to algae and higher plants by a two photosystem process. They lack nuclei and other organelles but possess peptidoglycan cell wall. All cyanobacteria contain chlorophyll a and mostly contain the blue phycobiliproteins phycocyanin and allophycocyanin giving their characteristic blue green color. Some cyanobacteria also contain phycoerythrin making the cells appear red. These phycobiliproteins are located in structures called phycobilisomes on the thylakoid membrane. They are an efficient light guides for the transfer of solar energy captured from sunlight. Although they lack membrane bound organelles as in eukarotic algae and higher plants they posses a variety of cellular structures and inclusions with specialized functions. In addition to this they also contain storage bodies which includes glycogen granules which store carbon and cyanophycin granules which store nitrogen. These inclusions allow cells to accumulate energy and nutrients under favourable condition and further use these reserves for maintenance and growth under stress conditions.

3 Commercial implications of cyanobacteria:

Cyanobacteria are an immense source of several metabolites such as alkaloids, flavanoids, phenols, carbohydrates, pigments, steroids, tannins, vitamins etc., cyanotoxins have been exploited as pesticides as they are known to have toxic effect. They are also enriched with pharmacologically active compounds that have effective antibacterial, anticancerous, antiviral, and antifungal properties. These cyanobacteria are employed in the production of biofuels which are cost effective and ecofriendly. The important constituents of biofuels such as carbohydrates, lipids and fatty acids are produced during the calvin cycle in cyanobacteria (Baroukh *et al.*, 2015). Among various applications biopolymer production from cyanobacteria is of recent trend because of its excellent properties similar to the currently available synthetic polymers but the major advantage that distinguishes it from the petroleum based polymer is that they are biodegradable (Fig.1).

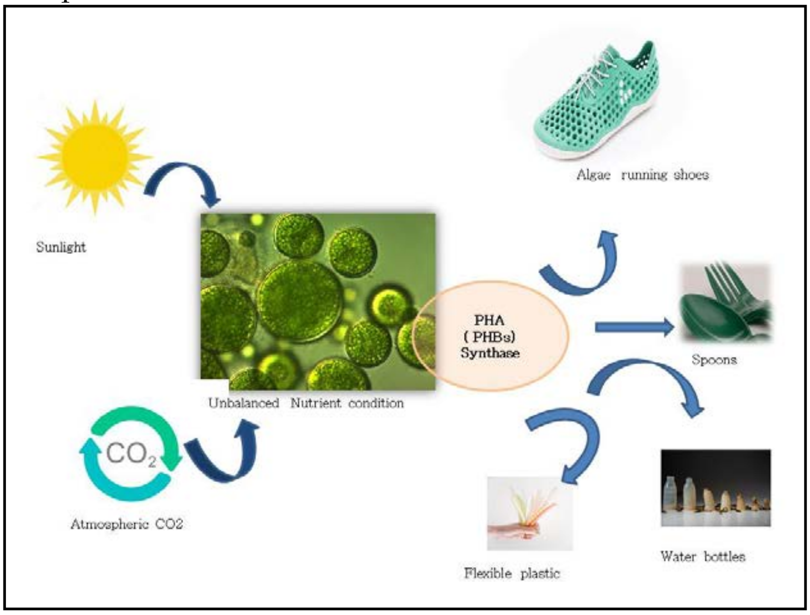

Fig.1 Algal Biopolymer commercial products

3.1 Polymers extracted from cyanobacteria:

Polyhydroxyalkanoate (PHA) are one of the most potential biopolymer which can be a better substitute for petroleum based polymer. PHA's are biodegradable biopolymers with similar characteristics as that of synthetic polymers due to their high molecular weight and other properties such as thermoplastic processability and hydrophobicity (Balaji *et al.*,2013) (Wu *et al.*,2001). PHA's are accumulated inside cell as insoluble granules for energy by various prokaryotic organisms. There are two species that have been reported to accumulate PHA, the chemoautotrophic bacteria and cyanobacteria known as blue green algae (Balaji *et al.*,2013) (Asada *et al.*,1999) (Sudesh *et al.*,2001). PHA can have various structure depending on conditions of organisms up to date 150 different structures of PHA have been identified some of the most well known are 3-hydroxypropionate, 3-hydroxybutyrate, 3-hydroxyoctonoate, 3-hydroxydecanoate, 3-hyroxydodecanoate, 3-tetradecanoate, 4-hydroxybutyrate (Balaji *et al.*,2013)

3.2 Cyanobacterial Poly-(hydroxybutyrate)(PHB):

Other than bacteria, cyanobacteria are potential PHA producers. Because cyanobacteria requires only minimal nutrient and can fix carbon dioxide as a sole carbon source. There are many advantages of using cyanobacteria over bacteria as PHA producing host as cyanobacteria use waste CO_2 and sunlight as their carbon and energy source and posses low production cost than bacteria. Therefore cyanobacteria are able to provide environmental friendly biopolymer that could be used effectively as bioplastic. However the PHA content in cyanobacteria is low in percentage cell dry weight compared to bacteria which may be attributed to large cell size and the cell wall of cyanobacteria being thicker that restrain downstream processing of PHA extraction (Sudesh *et al.*,2001). Among various PHA structures Poly-(hydroxybutyrate) is the most abundant type produced by blue green algae. PHB is a homopolymer of hydroxybutyrate that are present in various blue green algae such as *Chlorogloea fritschii*, *Spirulina* spp., *Aphanothece* spp., *Synechococcus* spp., *Gloethece* spp., *Synechocystis* sp, *Gloeocapsa* sp, *Spirulina platensis*, *Phormidium* sp etc.[30,31,32,35]. (Balaji *et al.*, 2013)) (Wu *et al.*,2001) (Asada *et al.*,1999) (Gopi *et al.*,2014).

Sabbir Ansari *et al.*, 2016 selected 23 cyanobacterial strains *Anabaena* sp., A.*variabilis*, *Aphanocapsa* sp., *Aulosira fertilissma*, *Calothrix brevisseima*, *Cylindrospermum* sp., *Hapalosiphon fontinalis*, *Michrochaeta* sp., *Nostoc sphaericum*, N.*muscorum*, N.*paludosum*, N.*punctiforme*, *Scytonema* sp., *Tolypothrix tenuis*, *Westiellopsis prolific*, *Chrococcus* sp., *Gleocapsa gelatinosa*, *Lyngbya* sp., *Oscillatoria* sp., *Phormidium* sp., *Plectonema* sp., *Spirulina platensis*, *Synechocystis* sp., for PHB production and found PHB with highest production in N.*muscorum* with 6.44%, N.*punctiforme* species with 6.27%, N.*paludosum*species with 6.10% and N.*sphaericum* with 6.12%. *Aulosira fertilissma* was the next highest PHB accumulator. Less production was observed in *Michrochaete* sp., *Hapalosiphon fontinalis*, *Westeillopsis prolific*, *Tolypothrix tenuis*, *Aphanocapsa*,etc., No PHB accumulation was noticed in *Cylindrospermum* sp.,

Manoj Singh *et al.*, 2019 examined PHB production in cyanobacterium *Scytonema geitleri* under varying environmental conditions such as pH, temperature and carbon sources. S.*geitleri* produced high quality PHB at pH 8.5 and temperature 30° C and acetate was the preferred carbon source.

Gopi *et al.*, 2014 isolated 15 cyanobacterial species from marine and fresh water resources for screening PHB producing strains and found 11 strains capable of producing PHB with *Phormidium* sp., producing 7.6% followed by *Synechococcus* sp with 4.5% *Synechocystis* sp with 3.7% and *Anabaena* sp with 2.3%. Among the selected strains *Phormidium* sp isolated from marine environment has been reported for PHB production for the first time.

Carpinea reported the successful production of PHB by *Synechocystis* sp PCC6803 just from CO_2 and the level of PHB production was enhaced by nitrogen starvation condition (Carpinea *et al.*, 2015)

Devadas explored the bioplastic PHB production using *Chlorella vulgaris* freshwater strains. The strains were screened by sudan black B and nile blue stain. The PHB production was optimized using different culture media and various parameters like aeration, effect of sodium acetate and phosphate etc., The PHB was extracted by hot chloroform and quantified by reading the absorbance at 235nm in UV spectrophotometer (Devadas *et al.*, 2020)

Motomu Nishioka *et al.*, 2001 examined that *synechococcus* sp.MA19 produced PHB when grown autotrophically under phosphate limited condition at 50° C.

Dulce Maria Arias *et al.*, 2018 revealed that cyanobacteria dominated cultures cultivated in wastewater effluent can be used as PHB producers. The effect of N and P limitation during two different photoperiods was evaluated for two weeks and the result showed highest PHB production under P limitation and constant illuminence. This study highlights that nutrient limitation could be a better approach in order to enhance the PHB accumulation in wastewater-borne cyanobacteria.

Monshupanee *et al*., 2016 utilized the easy to harvest cyanobacterium *Chlorogloea fritschii* using a two stage cultivation strategy. The cells were first pregrown under normal photoautotrophic condition to increase the biomass and recultivated under heterotrophic condition with a single organic substrate to produce the required product. Through this two stage cultivation method, the mass conversion of acetate to PHB was obtained.

Maheswari *et al*., 2011 prepared bioplastic using the cyanobacterium *Spirulina platensis* cultivated in Zarrouk medium. The medium was optimized by using sodium acetate to increase the PHB concentration. The S.*platensis* was measured for total dry weight and PHB by UV spectrophotometer before and after optimization of culture medium. The result showed little higher PHB content (6.20%) in S.*platensis* grown in optimized medium when compared with untreated one (5.18%). In addition the chemical based commercial plastic was prepared and compared with the bioplastic. From the comparision study the plasticizing and moldable property was good in all plastics. But the biodegradation was considered to be better in bioplastic due to the presence of PHB.

Keerati Taepucharoen *et al*., 2017 found photoautotrophically grown cyanobacterium *Oscillatoria okeni* to produce bioplastic (PHBV) under nitrogen deprivation. The heterotrophically grown cells under light showed no increase of PHBV but an increased production was observed under dark condition.

Shilalipi Samantaray *et al*., 2012 identified a phototrophic N2 fixing cyanobacterium, *Aulosira fertilissima* as a potential source for the production of PHB biopolymers. PHB accumulation upto 66% cell dry weight was observed when the cells are cultured in acetate with citrate supplemented medium. Also *Aulosira* culture supplemented with 0.5% citrate under phosphate deficiency depicted a PHB accumulation of 51% when incubated in dark for five days period. PHB accumulation was found to reach upto 77% under P deficiency with 0.5% acetate supplementation. The optimization of process parameters by response surface methodology resulted in PHB accumulation upto 85% at 0.26% citrate, 0.28% acetate and 5.58 mgL-1 dipotassium hydrogen phosphate for a five days incubation period. The A.*fertilissima* cultures pre-grown in fructose supplemented BG11 medium when subjected to the optimized culture condition the PHB accumulation boosted up to 50 folds higher than the control. A.*fertilissima* is the first cyanobacterium where the PHB accumulation reached up to 85% under nutrient manipulation and optimization and also the polymer exhibited similar material properties when compared with the commercial polymer.

Laxuman Sharma *et al*., 2006 found out the interactive effects of four variables viz. concentrations of acetate, glucose, dipotassium hydrogen phosphate and dark incubation on PHB production in a nitrogen fixing cyanobacterium Nostoc muscorum. Acetate, glucose and dark incubation exhibited positive impacts on PHB accumulation and yield.

Sandra Mareike *et al*., 2012 explored that the cyanobacterium *Nostoc muscorum* is a PHB accumulator which is considered one of the potential raw material supplier because of their short generation cycles. A range of experimental conditions have been examined such as phosphate starved cells with the addition of external carbon sources. The highest accumulation of PHB was observed in a phosphate starved culture medium with 1% glucose and 1% acetate. After 23 days 1L of culture contained upto 145.1 mg of PHB in phosphate starved medium. Aeration and CO2 addition resulted in highest PHB accumulation.

Campbell *et al.*, 1982 identified PHB in the cyanobacterium *Spirulina platensis*. The reduced carbon compounds addition was not required for PHB accumulation. PHB accumulated upto 6% of total dry weight during the exponential growth and seemed to decrease during the stationary phase.

Hanan H Omar *et al.*, 2016 performed experiments with three cyanobacterial PHB producers *Oscillatoria salina*, *Anabaena cylindrical* and *Nostoc linckia* and determined PHB production after 7, 14 and 21 days. The highest dry weight was observed at stationary phase and PHB accumulation were known to increase with increasing dry weight upto 14 days and then declined after 21 days. The pH values between 8 and 9 were preferred for better accumulation of PHB. The strains accumulated highest PHB at pH 8. Nitrogen and Phosphate starvation were found to be a stimulatory for PHB production. It was concluded that cyanobacteria are capable to synthesize high PHB under stress conditions.

Roberto De Philippis *et al.*, 1992 described the effect of different growth conditions on glycogen and PHB accumulation in the cyanobacterium *Spirulina maxima*. It was found that under photoautotrophic conditions S.*maxima* exhibited glycogen content of 7.1 without nutrient limitation and PHB was undetectable. While under mixotrophic conditions in the presence of acetate the PHB content increased to more than 3% of dry weight and during nitrogen starvation PHB remained low. The addition of azaserine induced glycogen accumulation but did not stimulate PHB synthesis. Phosphorous limited condition resulted in glucogen and PHB accumulation upto 23% and 1.2%. shifting culture from low to high light induced rapid glycogen accumulation but not PHB.

Massimo Vincenzini *et al.*, 1990 depicted the occurrence of PHB in several strains of photoautotrophically grown *Spirulina* spp. In the presence of acetate under mixotrophic condition the level of PHB accumulation reached values greater than 2.5% of dry weight but no significant effect was obtained with pyruvate.

Researchers also tested various cyanobacterial strains for PHB accumulation but all showed varying amounts with *Nostoc* sp and *Calothrix* sp with maximum accumulation. The heterocystous species produced PHB upto 11% and 10% of dry cell weight when photoautotrophically grown. The PHB accumulation enhanced to 15-20% or 17-24% in *Nostoc* sp and 12-19% or 12-16.4% in *Calothrix* sp after 21 days under mixotrophic and chemoheterotrophic conditions with varying concentrations of glucose, fructose, maltose and acetate. The presence of acetate resulted in maximum PHB in *Nostoc* sp but *Calothrix* sp showed maximum PHB accumulation in the presence of fructose content followed by acetate. Phosphate starvation also increased PHB accumulation in both strains.

Bhabatarini Panda, 2008 investigated the PHB accumulation in unicellular cyanobacterium *Synechocystis* sp PCC 6803. Under photoautotrophic condition it was found to accumulate the homopolymer of PHB with a maximum value of 4.5% dry cell weight and in addition the effects of various cultural and nutritional conditions were studied. PHB accumulation was found to be stimulated by nitrogen and phosphorous deficient conditions. Also chemoheterotrophy and mixotrophy under gas exchange limitations enhanced PHB yield upto 22 and 30%.

Tugarova aimed to increase the PHB accumulation using stress conditions such as nitrogen deficiency and osmotic stress (Tugarova et al., 2021). Sixty Thailand isolated strains of cyanobacteria and *Synechocystis* sp.PCC 6803 was cultured under stress conditions but the osmotic stress reduced PHB levels in all strains. The high PHB accumulator *Synechocystis* has been selected for PHB production under nutrient deficiency. The absence of N or P is the optimal condition for maximum accumulation of PHB in *Synechocystis* sp. (Khetkorn *et al*., 2016) But reduced nitrogen decreased biomass production whereas decreased phosphorous did not affect the biomass.

4. Conclusion

The world is marching towards the sustainable approach by synthesising green based materials or products to combat the detrimental effects caused by the petrochemical derivatives for several decades. Algal biopolymer is one such an alternative to meet out the huge demand in terms of cost, degradability and non-toxic effects.

6. References

Alyssa Mertes. (2019). What are the different types of plastics? https://www.qualitylogoproducts.com/promo-university/different-types-of-plastic.htm

Anne Marie Helmenstine. (2019). What is a Polymer? https://www.thoughtco.com/definition-of-polymer-605912.

Araujo, D., Ferreira, I. C., Torres, C. A., Neves, L., & Freitas, F. (2020). Chitinous polymers: extraction from fungal sources, characterization and processing towards value-added applications. *J. Chem. Technol. Biotechnol.*, **95(5):** 1277-1289.

Asada, Y., Miyake, M., Miyake, J., Kurane, R., & Tokiwa, Y. (1999). Photosynthetic accumulation of poly-(hydroxybutyrate) by cyanobacteria—the metabolism and potential for CO2 recycling. *Int. J. Biol. Macromol.*, **25(1-3):** 37-42.

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(3):** 278-285.

Baroukh, C., Muñoz-Tamayo, R., Steyer, J. P., & Bernard, O. (2015). A state of the art of metabolic networks of unicellular microalgae and cyanobacteria for biofuel production. *Metab. Eng.*, **30:** 49-60.

Benabid, F. Z., & Zouai, F. (2016). Natural polymers: Cellulose, chitin, chitosan, gelatin, starch, carrageenan, xylan and dextran. *Alger. J. Nat.*, **4(3):** 348-357.

Rehm, B. H. (2010). Bacterial polymers: biosynthesis, modifications and applications. *Nat. Rev. Microbiol.*, **8(8):** 578-592.

Bhabatarini Panda. (2008). Accumulation of Polyhydroxyalkanoates In A Unicellular Cyanobacterium Synechocystis. *Biol Macromol.*, **25:** 37-42.

Byrom D. (1987). Polymer synthesis by microorganisms: Technology and economics. Trends. *Biotech.*, **5:** 246-250.

Campbell J III., Stevens SE., & Balkwill. (1982). Accumulation of poly-beta-hydroxybutyrate in *Spirulina platensis*. *J. Bacteriol.,* **149(1):** 361-363.

Cybulska, J., Halaj, M., Cepák, V., Lukavský, J., & Capek, P. (2016). Nanostructure features of microalgae biopolymer. *Starch-Starke,* **68(7-8):** 629-636.

Devadas, V. V., Khoo, K. S., Chia, W. Y., Chew, K. W., Munawaroh, H. S. H., Lam, M. K. & Show, P.L. (2021). Algae biopolymer towards sustainable circular economy. *Bioresour. Technol.,* **32**: 12-22.

Ozçimen, D., Inan, B., Morkoç, O., & Efe, A. (2017). A review on algal biopolymers. *J. Chem. Eng. Res. Updat.,* 4: 7-14.

Ellis, B., & Smith, R. (Eds.). (2008). *Polymers: a property database.* CRC press.

Gopal Rao M., Bharathi & Akila RM. (2014). A Comprehensive Review On Biopolymers. *Sci. Revs. Chem.Commun*., 4(2),61-68.

Gopi K., Balaji S., & Muthuvelan B. (2014). Isolation purification and screening of Biodegradable Polymer PHB Producing Cyanobacteria from Marine and Freshwater Resources. *Iranica J. Energ. Env.,* **5(1):** 94-100.

Gowthaman, N. S. K., Lim, H. N., Sreeraj, T. R., Amalraj, A., & Gopi, S. (2021). Advantages of biopolymers over synthetic polymers: social, economic, and environmental aspects. *Biopoly. Industr. Appl.* 12: pp. 351-372.

Hanan H Omar., Magda M Aly., Wasayf J Al-Malik., & Khaled S Balkhair. (2016). Production and enhancement of poly-β-hydroxybutyrate in cyanobacteria. *Main Group Chem.,* **15(2):** 153-161.

Hassan Namazi. (2017). Polymers in our daily life. *Bioimpacts.*7(2):73-

Hazer B. & Steinbuchel A. (2007). Increased diversification of polyhydroxyalkanoates by modification reactions for industrial and medical applications. *Appl. Microbiol. Biotechnol.,* 74(1): 1-12.

Jansen, J. A. (2016). Plastics–It's All About Molecular Structure. *Plast Eng Plastics Engin.,* **72(8):** 44-49.

John Masani Nduko Seiichi Tguchi. (2019). Microbial production and properties of LA-based polymers and oligomers from Renewable feedstock. Production of Materials from Sustainable Biomass Resources pp 361-390.

Keerati Taepucharoen., Somchai Tarawat., Monthira Puangcharoen., Aran Incharoensakdi., & Tanakarn Monshupanee. (2017). Production of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) under photoautotrophy and heterotrophy by non-heterocystous N2 fixing cyanobacterium. *Bioresour. Technol.,* **239:** 523-527.

Khetkorn, W., Incharoensakdi, A., Lindblad, P., & Jantaro, S. (2016). Enhancement of poly-3-hydroxybutyrate production in Synechocystis sp. PCC 6803 by overexpression of its native biosynthetic genes. *Bioresour. Technol.*, **214:** 761-768.

Kim SK., & Chojnacka K. (2015). Marine Algae Extracts. *Chapt.,* **26:** 454-456.

Kunal., & Anita Rajor. (2011). Microbial Polymers: An Alternative to future Plastics.

Kusum Kaushik., Ram Babu Sharma., Shweta Agarwal. (2016). Bioplastics and its uses**.** *Int. J. Pharmaceut. Sci. Rev. Res.,* **37(2):** 30-36.

Laxuman Sharma ., Akhilesh Kumar Singh., Bhabatarani Panda., & Nirupama Mallick. (2006). Process optimization for poly-b-hydroxybutyrate production in a nitrogen fixing cyanobacterium, Nostoc muscorum using response surface methodology.

Lenz R.W., & Marchessault R.H. (2005). Bacterial polyesters: Biosynthesis, biodegradable plastics and Biotechnology, *Biomacromol.,* **6:** 1-8.

Manoj K.Singh., Pradeep K.Rai., Surendra Singh., & Jay Shankar Singh. **(2019)**. Poly-β-Hydroxybutyrate Production by the Cyanobacterium Scytonema geitleri Bharadwaja under Varying Environmental Conditions. *Biomol.,* **9(5):** 198-1-210.

Massimo Vincenzini., Claudio sili., Philippis R De., Alba Ena., & Richardo Materassi. (1990). Occurrence of poly-beta-hydroxybutyrate in Spirulina species. *J. Bacteriol.,* **172(5):** 2791-2792.

Mclntosh M., Stone B.A & Stanisich V.A. (2005). *Appl.Microbiol. Biotechnol***.,** **68:** 163-164.

Meyer A. (1904). Orientierende Untersuchungen ueber Verbreitung, Morphologie, and Chemie des volutins. *Bot. Zeit.,* **62:** 113-152.

Motomu Nishioka., Katsuya Nakai., Masato Miyake., Yasuo Asada., & Masahito Taya. (2001). Production of poly-β-hydroxybutyrate by thermophilic cyanobacterium, Synechococcus sp. MA19, under phosphate- limited conditions. *Biotechnol. Lett.,* **23:** 1095-1099.

Namazi, H. (2017). Polymers in our daily life. *BioImpact.,* **7(2):** 73-74.

Ozdemir N., & Erkmen J. (2013). The Black Sea. *J. Sci.,* **3(8):** 89-104.

Carpine, R., Olivieri, G., Hellingwerf, K., Pollio, A., & Marzocchella, A. (2015). The cyanobacterial route to produce poly-β-hydroxybutyrate. *Chem. Eng. Trans*, 43: 289-294.

Sandra Mareike Haase., Bernhard Huchzermeyer., & Thomas Rath. (2012). PHB accumulation in Nostoc muscorum under different carbon stress situations. *J. Appl. Phycol.*, 24(2): 157-162.

Seviour R.J., Stasinopoulos S.J., & Auer D.P.F. (**1992**). *Crit.Rev.Biotechnol.,*12: 279-282.

Shilalipi Samantaray., & Nirupama Mallick. (2012). Production and characterization of poly- β - hydroxybutyrate (PHB) polymer from Aulosira fertilissima. *J. Applied Phycol.,* 24(4): 803-814.

Mohan, S., Oluwafemi, O. S., Kalarikkal, N., Thomas, S., & Songca, S. P. (2016). Biopolymers–application in nanoscience and nanotechnology. *Rec. Adv. Biopoly.*, **1(1): 47-66.**

Sudesh K., Taguchi K., & Doi Y. (2001). Can cyanobacteria be a potential PHA producer?

Tan D., Yin J., & Chen GQ. (2017). Production of Polyhydroxyalkanoates. Current Developments in Biotechnology and Bioengineering Production. Isolation and purification of Industrial product, Elsevier. 655-692.

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. *Scient. Report.*, 6(1): 1-9.

Tugarova, A. V., Dyatlova, Y. A., Kenzhegulov, O. A., & Kamnev, A. A. (2021). Poly-3-hydroxybutyrate synthesis by different Azospirillum brasilense strains under varying nitrogen deficiency: A comparative in-situ FTIR spectroscopic analysis. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 252, 119458.

Thompson, R. C., Swan, S. H., Moore, C. J., & Vom Saal, F. S. (2009). Our plastic age. Philosophical Transactions of the Royal Society B: *Biol. Sci.*, 364: 1973-1976.

Maheswari, N. U., & Ahilandeswari, K. (2011). Production of bioplastic using Spirulina platensis and comparison with commercial plastic. Res. Environ. *Life Sci.*, **4(3):** 133-136.

Wu GF., Wu QY., & Shen ZY. (2001). Accumulation of poly-β hydroxybutyrate in cyanobacterium Synechocystis sp.PCC6803. Bioresour. *Technol.*, **76:**85-90.