Indian Journal of Advances in Chemical Science

Review Article

Production of Bioplastics: A Sustainable Development

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ABSTRACT

Plastic pollution is a global problem that degrades the environment and subsequently kills animals. New research lines are emerging to find highly biodegradable bioplastics or plastic compositions that are more ecologically friendly than present ones. Bioplastic forms a rapidly growing class of polymeric materials that can be manufactured from vegetable oils and starch and also by exploiting microorganisms. Microorganisms have the feature of producing different biopolymers like polyhydroxyalkanoates (PHAs) naturally. These microorganisms can be utilized to develop strategies for using them as cell factories. These biopolymers are accumulated inside the microorganisms as energy reserves of carbon. Extremophiles like haloarchaea species show the production of considerable amounts of PHA, polyhydroxy butyrate, and polyhydroxy valerate. Studies also suggest that microalgae and cyanobacteria are also the two promising sources of PHAs. This review is focusing on the production of bioplastics from microalgae, summarizes the production of bioplastics from haloarchaea and followed by covering the advantages of lignocellulosic fibers and lignin in bioplastics.

Key words: Bioplastics, Polyhydroxyalkanoates, Polyhydroxy butyrate, Polyhydroxy valerate, Lignocellulosic fibers, Lignin.

1. INTRODUCTION

Plastic pollution is increasing day by day and synthetic plastics entered into the food web thus its biomagnifications harming the human as well as animal health. As a result, new advanced findings are emerging to develop biodegradable plastics and bioplastic formulations that are more eco-friendly than existing ones. Both scientific and political communities have emphasized the necessity to find alternative biodegradable polymers that replace the use of existing plastic materials. Bioplastics are a type of plastic made from sustainable biomass sources, as opposed to plastics from petroleum, a fossil fuel. Bioplastics are having the efficiency to biodegrade into organic compounds by microorganisms such as bacteria, fungi, and algae, on account of this, bioplastics offer an environmentally friendly replacement to synthetic plastics [1]. Bioplastics are polymers manufactured by microorganisms. Microorganisms accumulate biopolymers intracellularly in their granules as carbon and energy reserves, this cellular process is powered by sugar derived from plant feedstocks [2]. Biopolymers and oligomers can be produced from the fermentation of renewable plant biomass sources. During the fermentation process, the buildup of polymers within the bacteria takes place in a bioreactor. The polymer from the microorganisms is recovered using a process that includes centrifugation to isolate the bacteria followed by press filtering and drying of the resulting bioplastic [3]. Polyhydroxyalkanoates (PHAs) are the most frequently investigated bioplastics created by this technique. PHAs are the well-studied forms of microorganisms-generated polyesters. Poly(hydroxybutyrate) (PHB) and poly(hydroxyvalerate) (PHV) are the two most frequent types of PHA (PHV). Because of the variety of monomers that microbes can polymerize, PHAs have the potential to be competitive bioplastic. Poly-(R)-3-PHB, the copolymer of (R)-3- hydroxybutyrate (3HB) and (R)-hydroxyvalerate (3HV) termed PHBV, and the copolymer of (R)-3-hydroxybutyrate (3HB) and (R)-hydroxyhexanoate (3HHx) termed PHBHHx are examples of commercially available PHAs [4]. Because of their low mechanical strength, bioplastics have been used only in limited applications [5]. Synthetic fibers such as glass and carbon fibers are often utilized as reinforcements in bioplastics. Compared to synthetic fibers, lignocellulosic fibers are renewable, biodegradable, and abundantly available resource. Those fibers are low-density fibers, having better mechanical properties, and are reasonably inexpensive [6]. Sugarcane bagasse, wheat straw, rice straw, forest wood (the hemp), kenaf, flax, and other lignocellulosic fibers have all been utilized as reinforcements in bioplastics. Lignin-reinforced bioplastics have recently piqued the interest of scientists all around the globe. Lignin is the most abundant natural aromatic material after cellulose in terms of plant biomass abundance [7].

2. BIOPLASTIC PRODUCTION FROM MICROALGAE

Microalgae and cyanobacteria are two of the most promising sources of bioplastics as they are made up of components such as PHA, cellulose, and protein which can be used in bioplastics production.

2.1. PHA in Microalgae

PHA is produced by algae cells as an internal carbon source from carbohydrates and lipids [8]. Microalgae can convert atmospheric carbon dioxide into PHA without the use of any other carbon source. Microalgae are advantageous as they compensate for the increasing emission of CO_2. Severe thermal stress and nutrient limitation lead to an increase in PHA content in microorganisms [9-13]. Miyake *et al.*

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ISSN NO: 2320-0898 (p); 2320-0928 (e)
DOI: 10.22607/IJACS.2021.904023

Received: 09th October 2021;
Revised: 17th October 2021;
Accepted: 22nd October 2021

have shown that PHA level can be increased to 27% in *Synechococcus* sp. under nitrogen deprivation [11]. Sharma *et al.* also observed that level of P (3HB) increased up to 23% under phosphate limitation [12]. Finally, there was a 77% increase in P(3HB) in *Aulosira fertilissima* CCC 444 under phosphorus limitation in the presence of fructose and valerate has also been proved [13]. The blending of polymers with PHA was shown to improve the properties of PHA as they have low strength. Various biodegradable polymers such as cellulose, lignin, poly(lactic acid) (PLA), and polycaprolactone have been proven to improve the properties of PHA when it is incorporated as PHA mixtures [9]. Some traditional modifiers such as plasticizers and mineral fillers are also used to improve the tensile strength and toughness of the final material. The thermal stability of PHA can also be increased by blending with synthetic or natural rubber as showed by Bhatt *et al*. [10].

2.2. Microalgal Proteins

Wang *et al*. developed a method to produce algal bioplastics by protein modification of catfish algae and protein-rich microalgae (nanochloropsis) [14]. However, the catfish algae bioplastic showed a stiff behavior while the latter one was more flexible. Wang *et al.* also introduced an innovative system to bring out bioplastic from *Spirulina* biomass [14].

2.3. Microalgal Starch

Mathiot *et al.* established a method of using microalgae starch in bioplastic production and starch is one of the most extensively used biopolymers as a replacement for traditional plastics. However, it appears to have a disadvantage in terms of water resistance and mechanical strength. Microparticle or nanoparticle reinforcements have been added into starch to overcome these inherent flaws. These interactions considerably improved the features of the resulting bionanocomposites. Starch content in microalgae can be increased by nitrogen, phosphorus, and sulfur limitation [15]. An increase in light intensity also causes an increase in starch production in microalgae [16].

2.4. Microalgal Cellulose

Mithranyan showed that cellulose derived from *Cladophora* sp. can be used in bioplastic production [17]. *Cladophora* cellulose nanofiber composite was generated by coating the fibers with polypyrrole polymers. Morais *et al.* produced nanocellulose biocomposites with a diameter of 110 nm [17].

3. BENEFITS OF USING HALOARCHAEA BIOPLASTICS

PHA/PHB manufacturing on a large scale is a costly process as it involves the use of organic solvents in the downstream process [18]. Mesophilic bacteria which were used to produce the biopolymers are more susceptible to contamination than extremophilic bacteria. Extremophiles have recently been identified as the most successful microbes for producing PHA and they potentially lower the manufacturing costs [18]. Halophytic microorganisms have several benefits over non-halophytic microbes. Cell lysis is a very simple process in halophytic microorganisms they get lyses easily when exposed to distilled water. The halophytic bacterial population has many other advantages too: Many haloarchaeal species grow quickly compared to other microbial strains; sterilization is not required. The majority of halophilic archaea discovered so far can produce PHBV from structurally unrelated carbon sources, such as starch, glucose, and glycerol [19]. PHA is produced by haloarchaea genera such as *Halococcus, Haloferax, Halorubrum, Halobacterium, Natronobacterium, Natronococcus, Halopiger,* and *Haloarcula*, according to several research works reported in the area [20,21].

3.1. Species of Haloarchaea Capable of Producing PHA, PHB, and PHV

Kirk and Ginzburg (1972) revealed PHA accumulation in haloarchaeal cells from *Halobacterium* sp. (now known as *Haloarcula marismortui*). PHB was discovered in three *Haloferax* species (*Haloferax mediterranei, Haloferax volcanii,* and *Haloferax gibbonsii*) and *Haloarcula hispanica* by Fernandez-Castillo *et al.* in 1986 [22]. PHA build-up was also reported in two additional *Haloarcula s*pecies (*Haloarcula vallismortis* and *Haloarcula Japonica)* [23,24]. PHA makers include two species of *Haloquadratum walsbyi*, as well as others from the genera *Halostagnicola, Haloterrigena, Halobiforma, Haloarcula, Halobacterium, Halococcoccus, Halorubrum, Natrinema,* and *Haloalkaliphiles* such as *Natronobacterium* and *Natronococcus*. *Halorubrum lacusprofundi*, the third most common species in Antarctica's Deep Lake, was recently verified to generate PHA-like granules at low temperatures. Due to its fast growth rate, metabolic flexibility, genetic stability, and excellent transformation mechanism, *H. mediterranei* is perhaps the most desired PHA generator among all haloarchaeal strains. Many species require a precursor (3HV) for PHBV synthesis, but *H. mediterranei* can synthesize PHBV effectively without one and it will reduce the cost of production. Furthermore, in the presence of 4HB precursors in the media, *H. mediterranei* may synthesize other polymers of PHA like poly(3-hydroxybutyrate-co-3-hydroxyvalerate-co-4-hydroxybutyrate) (PHBV4HB) (Y-butyrolactone) [25,26].

3.2. The Influence of Cultivation Conditions on PHA Production in Haloarchaea

An excess of carbon substrate and a deficiency of other essential nutrients such as nitrogen and phosphorus can stimulate the organism to produce the storage granules with PHA. Many microbes and plants use this stress response to adapt to their surroundings. Great efforts are going on to reduce the cost of production of PHA by using low-cost raw materials like Industrial waste as their carbon source [26].

3.3. Structural Properties of Bioplastic – PHA

PHA can be classified into two groups depends on the monomeric units. They are short-chain length PHAs (Scl-PHA) and medium-chain length PHAs (mcl-PHA) as shown in Figure 1. The scl-PHAs have 3–5 carbon atoms, some examples of them are 3-HB,4-HB, or 3-HV. These materials have more thermoplastic properties [27]. However, mcl-PHA comprises 6–14 carbon atoms. Examples of mcl-PHAs are 3-hydroxyhexanote (HHX) 3-hydroxyoctanate (HO) and it also includes long-chain monomeric units [27]. These mcl-PHAs have increased flexibility and reduced crystallinity but the purification and recovery process during solvent extraction is higher in scl-PHAs compared to mcl-PHAs [28]. Some of the approaches such as blending and functionalization of PHA polymers provide improved properties to PHA by increasing its applications [28].

4. LIGNIN IN BIOPLASTICS USAGE

Technical lignin is commercially accessible lignin derived through industrial delignification procedures. Technical lignins are from bulk feedstocks and are produced as a by-product of pulping or cellulosic ethanol production. The paper-making sector is a major source of technical lignin, with two major lignins: Kraft lignin (KL) and lignosulfonates. Although KL accounts for around 85% of global lignin production, lignosulfonates are the most significant commercially available lignin, with a yield of about 5%. Because it is sulfur free, this group is closer to lignin's natural structures. Organosolv lignin is lignin with fewer modifications and is mostly manufactured from processing hardwood and wheat straw [30]. Organosolv lignin has a higher homogeneity than lignosulfonates or KL [30].

4.1. Structure and Properties of Lignocellulosic Fibers and Lignin

Lignocellulosic fibers are made up of cellulose fibers in one or more layers and reinforced by a matrix of hemicelluloses altering in each layer [31]. Hemicellulose is made up of hydrogen-bonded cellulose molecules. The structure of cellulose-hemicellulose is then strengthened by lignin covalently bonded to hemicellulose, as shown in Figure 2. The hydrophobic lignin acts as a coupling agent, filling in the gaps between the cellulose and hemicellulose matrix. Nowadays lignin-carbohydrate complexes with varying compositions and structures are formed [32].

4.2. Lignin as a Bioplastic and its Types

The use of lignin as a reinforcement reduces cost and water absorption while increasing their mechanical properties. Lignin plays a key role in antioxidant capabilities as a stabilizer [33]. Following are the different types of lignin bioplastics: Starch-lignin bioplastics, protein-lignin bioplastics, cellulose-lignin bioplastics, PLA-lignin bioplastics, and PHB-lignin bioplastics PHB. When compared with other plastics, protein-based plastics have lower water absorption, thermal stability, and mechanical strength. In protein-derived plastics, to enhance their strength and water resistance, lignin has been used as a filler [34]. Cellulose and lignin individually provide separate properties to cellulose-lignin bioplastics. In general, cellulose fortifies the mechanical strength of the composites and lignin reduces water uptake, improves the thermal stability of the biopolymer matrix, and allows the even dispersion of cellulose. PLA is also a biodegradable and thermoplastic biopolymer having great mechanical properties and increased recyclability for industrial applications in bioplastics. The addition of lignin to PLA improves its thermal stability and tensile strength [35].

5. BIODEGRADATION OF BIOPLASTICS

5.1. Microorganisms that Degrade Bioplastics

Enzymes from microorganisms are having a crucial role in the enzymatic breakdown of bioplastics. Depolymerases derived from bioplastic-degrading microorganisms were proven to play an important role in the biodegradation of bioplastics [38]. *Streptomyces thermoviolaceus subsp. Thermoviolaceus 76T*-2 provided the depolymerase enzyme responsible for PCL breakdown. Bioplastics were used as a carbon source by a variety of microorganisms isolated from soil compost, soils, and farm hay [39]. *Stenotrophomonas, Penicillium, Aspergillus, Thermomyces, Fusarium, Clonostachys, Verticillium, Lecanicillium, Cladosporium, Mortierella,* and *Doratomyces* are bacterial and fungal species, isolated from compost environments and also *Actinobacteria* species such as *Amycolatopsis* and *Streptomyces* were the most common species of PHB degraders obtained from soil settings.

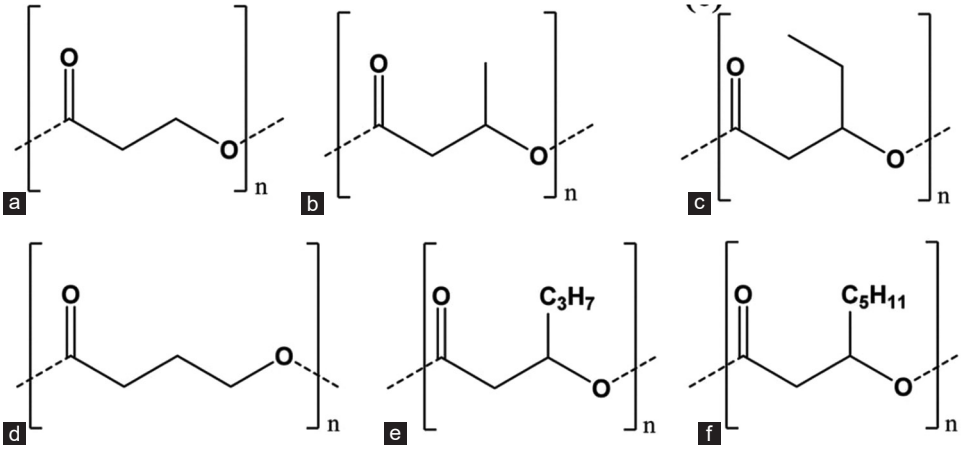

Figure 1: Structure of PHAs – (a)3-Hydroxypropionate (HP), (b) 3-hydroxybutyrate (HB), (c) 3-hydroxyvalerate (HV), (d) 4-hydroxybutyrate (4HB), (e) 3-hydroxyhexanoate (Hx), and (f) 3-hydroxyoctonaote (HO) chemical structures [29].

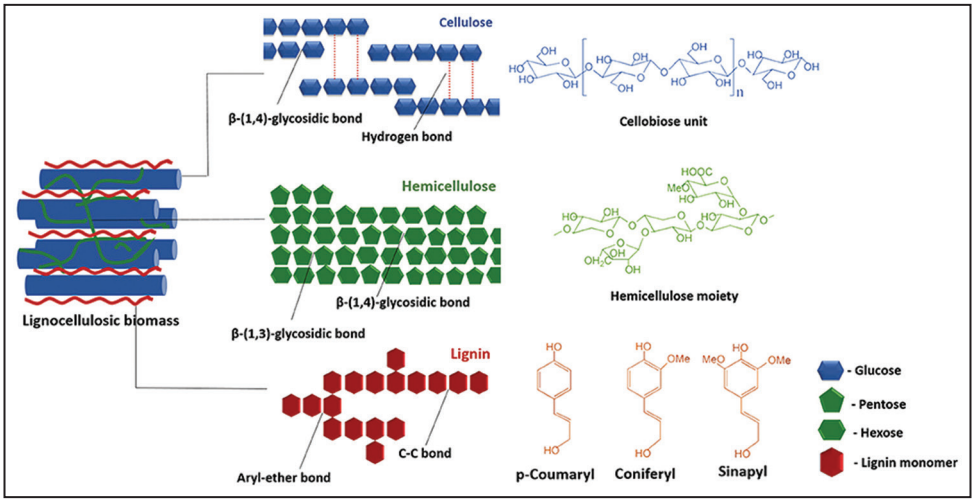

Figure 2: Outline of lignocellulosic plant biomass-lignocellulosic plant biomass has three main parts, cellulose, a homopolymer linked with glycosidic linkages (40–50 wt% of total mass), a heteropolymer-hemicellulose, has C_5 and C_6 sugars linked by glycosidic linkage (25–35 wt%) and aromatic heteropolymer lignin with phenylpropanoid units (15–20%) [36,37].

Paenibacillus, Pseudomonas, and *Bacillus* species were mainly identified from different soil environments and were capable of degrading the bioplastics. The strain SCM MK2 4 of *Amycolatopsis* sp. has the maximum enzymatic activity toward PLA and PCL bioplastics [40]. The most common microorganisms found to be capable of degrading bioplastics in aquatic systems, including marine and river water were bacterial species such as *Pseudomonas, Bacillus, Alvanivorax, Tenacibaculum, Lepthotrix, Enterobacter, Variovorax,* and *Gracilibacillus*. Other bioplastics, such as PLA, PHB, PBS, and PBSA, were not degraded by these strains. *S. thermonitrificans* has proven to show PCL bioplastic degradation. The same has also been experimentally demonstrated to exhibit an improved PCL bio-plastic degradation when it was co-cultured with *Bacillus licheniformis* HA 1 [41].

5.2. Bioplastics Biodegradation Under Various Environmental Conditions

Compostable plastic is always biodegradable, whereas biodegradable plastic is not always compostable [42]. Maize is a highly biodegradable substance, the incorporation of corn in PLA/corn bioplastic seems to improve compost biodegradation. As a result, bacteria were able to destroy the material and the PLA fraction more quickly [43]. Soil always has a large diversity of microorganisms, making bioplastic biodegradation more viable than in other environments such as water or air. The biodegradation of PHB/PPW-FR (potato peel waste – fermentation residue) biocomposite was shown to be more efficient than that of pure PHB because the PPW-FR fibers reduced the crystallinity of the PHB [44]. In aquatic systems, the water temperature could also affect bioplastics degradation. The rate of PHA film biodegradation was observed differently in various periods of the year due to changes in temperature of water. Different seawater might also affect bioplastics degradation due to differences in existing microorganisms [44]. The shape of polymer can also alter the biodegradation rate in marine water, it was observed that PHA films are degraded faster than PHA pellets because PHA films have comparatively larger surface area [45].

6. CONCLUSION

Biodegradable bioplastics are durable as other types of plastic, as they only break down in specific conditions. Bioplastics can be used as a sustainable alternative to synthetic plastics but still, they are used only around 1% of the whole world. There is still a need to focus on efficient strategies for bioplastic disposal. According to the studies, microbiological processes have the potential to replace traditional oil-based polymers. However, their downstream processing might not be economical. For PHA production, one should look for a better and cheap carbon source. There is also a need to investigate proper genetic modification that can be used to enhance the properties of algal bioplastics. In recent years, promising laboratory discoveries on haloarchaea-related PHA synthesis have been revealed but technoeconomic analyses are yet to be done. The research has to be accelerated to improve the upscaling of those promising processes from the laboratory to the industrial scale to accelerate the development of archaeal cell factories and demonstrate their potential for the future of sustainable bioplastics. The studies have also shown the architecture and properties of lignocellulosic fibers. Lignin has the potential to act as a plasticizer, stabilizer, or biocompatibilizer in bioplastics, resulting in a variety of characteristics. According to our review, more research into lignocellulosic fibers should be conducted without eliminating lignin while making bioplastics. Because of its availability as a by-product of varied origins from papermaking and ethanol production, the utilization of lignin in bioplastics has a bright future.

6. ACKNOWLEDGMENT

The authors are highly indebted to President, Principal, and to the Department of Biotechnology, Isabella Thoburn College, Lucknow, India, for their great support and encouragement to complete this manuscript.

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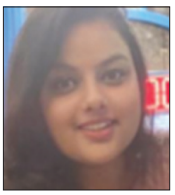

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