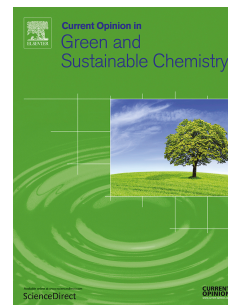


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Sustainability of Bioplastics: Opportunities and Challenges

SourbhThakur^{a,b*}, Jyoti Chaudhary^b, Bhawna Sharma^b, Ankit Verma^b, Sigitas Tamulevicius^a, Vijay Kumar Thakur^{c*}

^a*Institute of Materials Science of Kaunas University of Technology, Barsausko 59, LT-51423 Kaunas, Lithuania*

^b*School of Chemistry, Shoolini University, Solan 173212, Himachal Pradesh, India*

^c*Enhanced Composites and Structures Center, School of Aerospace, Transport and Manufacturing, Cranfield University, Bedfordshire MK43 0AL, UK*

Abstract

Recycling is groundwork of the worldwide efforts to diminish the amount of plastics in waste. Mostly around 7.8-8.2 million tons of poorly-used plastics enter the oceans every year. Non-biodegradable plastics settlements in landfills are uncertain, which hinders the production of land resources. Non-biodegradable plastic solid wastes, carbon dioxide, greenhouse gases, various air pollutants, cancerous polycyclic aromatic hydrocarbons and dioxins, released to the environment cause severe damage and harmfulness to the inhabitants. Due to the bio-degradability and renewability of biopolymers, petroleum-based plastics can be replaced with bio-based polymers in order to minimize the environmental risks. In this review article, bio-degradability of polymers has been discussed. The mechanisms of bio-recycling have been particularly emphasized in the present article.

Keywords: Plastic solid waste; land filling; bioplastics; bio-degradation, bio-recycling.

*Corresponding authors Email: thakursourbh@gmail.com, vijay.kumar@cranfield.ac.uk,
sourbh.sourbh@ktu.lt

Introduction

Plastic materials are widely used in our daily life and their usage in textiles, electronics, healthcare products, toys and in packaging applications are unavoidable [1–3]. Synthetic plastic is made up of artificial or semi-artificial organic compounds, which are flexible in nature. Since 1940s, synthetic plastics have reformed the society due to their fascinating properties like mechanical strength, lightness, flexibility and durability, these properties assigned to a material of low cost and ability to replace products made from other materials including paper, glass and metals [4]. In 2015, worldwide annual construction of petroleum contained plastic increased to 300 million tons [5]. According to [6], 34 million tons of plastic waste was produced per year and 93 % of material was dumped into oceans and landfills. Degradation of plastic is very difficult, during this process, there is emission of large amount of CO₂ and many other toxic compounds [7]. It is estimated that about 2.8 kg of CO₂ is evolved on burning 1 kg of plastic [8]. The emergence of bio-plastic arises due to the environmental considerations on the non-biodegradable plastic. The origin of bioplastic (biodegradable plastic) are cellulose, starch, sugar etc., which are primarily renewable in nature [9]. Biodegradable plastic is degraded by the natural microorganisms such as bacteria, algae, and fungi [10] (**Figure 1**). Its degradation depends on the environment conditions (temperature, water, oxygen) and chemical conditions of the polymer. In degradation of bioplastic, CO₂ emission is very low which emphasize the production of biodegradable plastic day by day [11]. In fact, 1.7 million tons of biodegradable

plastic was manufactured globally in 2014 and the manufacturing of biodegradable plastic is predicted to arrive 6.2 million tons in 2018 [12].

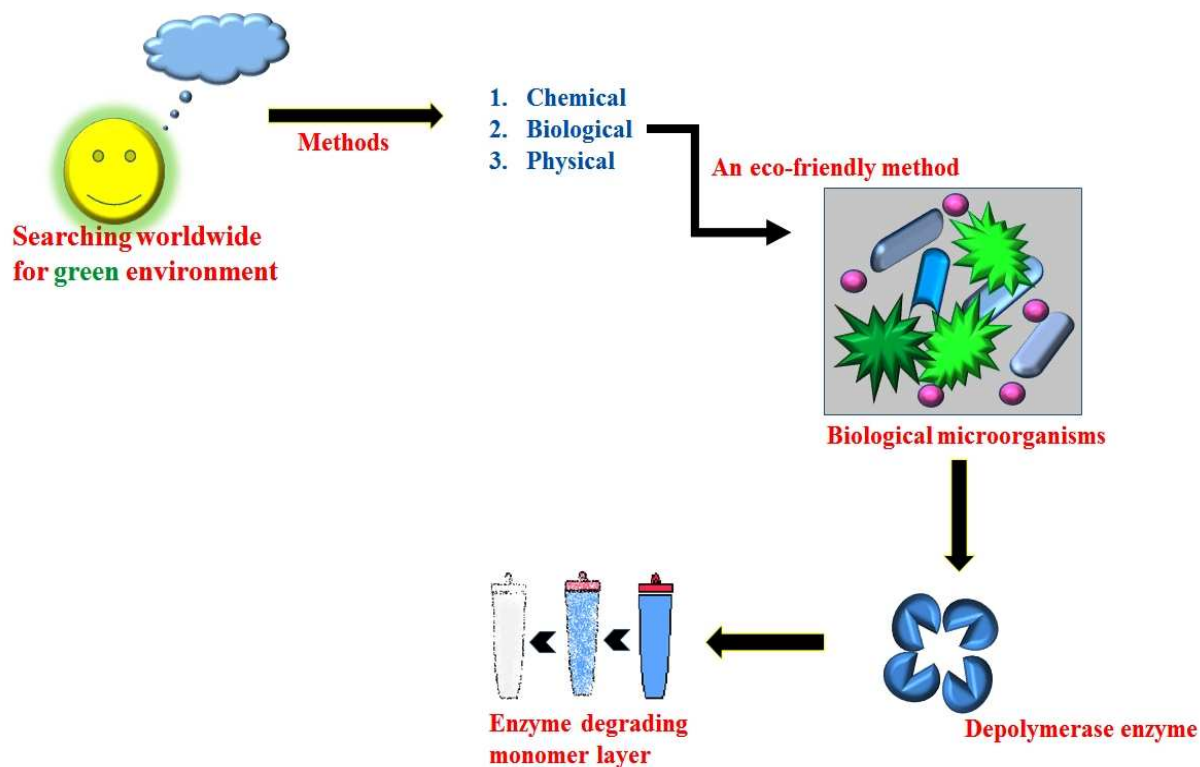


Figure 1. Schematic representation for degradation of bioplastic by enzyme.

No doubt, biodegradable plastics are environment-friendly but they also came with some limitations like high manufacturing cost and low mechanical tendency [13–15]. The decrease in the availability of gasoline and diesel due to the increase in cost increases the scarcity of resources which promotes the need for alternative methods of creating bioplastic [16]. In past few years, government councils have set the various standards to reduce the use of non-biodegradable plastic and in addition to this many scientific communities have tried to develop biodegradable materials like polylactic acid, polyhydroxyalkanoates, starch-based bioplastic and

many more [17]. It is better to use bio-renewable resources to generate plastic because their biodegradable period makes them most acceptable materials [18–20]. This review article concisely summarizes the biodegradability and renewability aspects of plastic based solids.

Biodegradability

Recently, bio-degradation of different bioplastics has been studied. Biopolymers catches the greater attention in market because they meet the basic requirements of life cycle environmental impact or life cycle assessments for its proper disposal [1] (Figure 2).

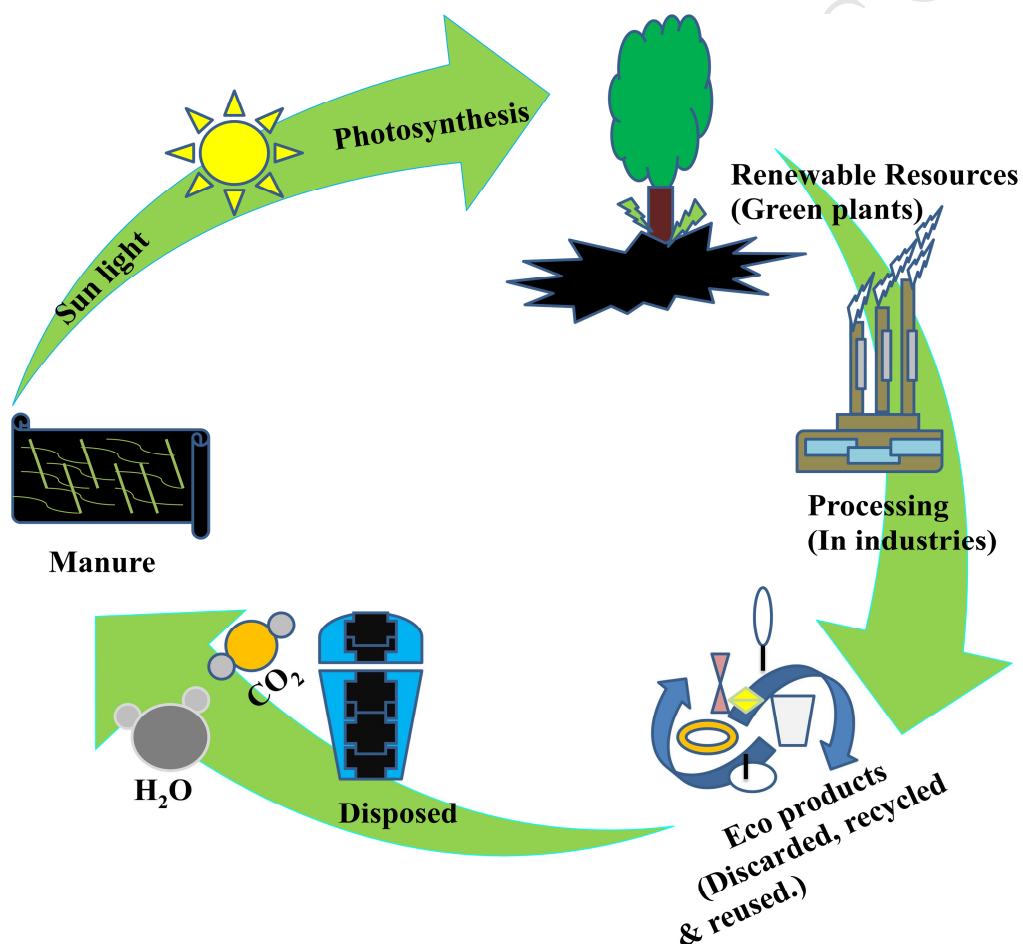


Figure 2. Proposed presentation for reuse of bioplastic through photosynthesis.

In comparison to conventional plastics, some bio-plastics like poly-lactic acid or polyhydroxyalkanoates requires few years for degradation but unfortunately, these bio-plastics are of high cost. One exceptional way to minimize cost is to blend them with natural bio-materials. Chin-San Wu evaluated the cheaper sisal fibers mixed grafted polylactide composite, high degradation rate was observed in sisal fibers mixed grafted polylactide composite as comparison to polylactide [21].

The biodegradability and composability are standardized by some specifications and test methods [5]. Non-biodegradability of petroleum-based synthetic plastic leads to the gathering of more plastic waste which promotes the major environmental impacts like global warming potential, carcinogenic, ozone depletion, eco-toxicity and eutrophication [22]. Accumulation of huge amount of plastic waste in environment forces many industrial fields to generate biodegradable plastic [23]. Biodegradability of these prepared polymers follows three key steps: biodeterioration, biofragmentation and assimilation [24]. Most reported biopolymers are poly lactic acid, polyhydroxyalkanoates, thermoplastic starch and plant-based materials [8]. Degradability and renewability of different polymers are represented in **Figure 3** [25,26]. There are some impact factors such as chemical structure, polymer chains, functional groups and crystallinity of biopolymers which affects their bio-degradation rate in environment [27]. In addition, more environmental factors like temperature, pH, oxygen content are also considered in bio-degradation of polymers [28,29]. Most plant based materials for example 1,3-propnediol and bio-polyethylene tetraphthalate and petroleum-based bioplastics including poly lactic acid, polyhydroxyalkanoates and many more are venerable for degradation by compost under microbial conditions [30]. However, time duration for degradation may vary from material to material. Poly lactic acid bioplastic showed very slow degradation and it lasts about 11 months

[31]. To improve the biodegradability, compost is mixed with biofuel byproducts [11]. Recently, it was reported that bio-degradation of cellulose acetate bioplastic was 44-35 % after 14 days of composting [32]. Bio-degradation of these materials varies in different systems like in aquatic systems or in soil systems. In aquatic system degradation mainly depends on water temperature and the shape of the polymer [33]. Whereas, greater than 90 types of bacterial and microbial activities are responsible for degradation in different ecosystems.

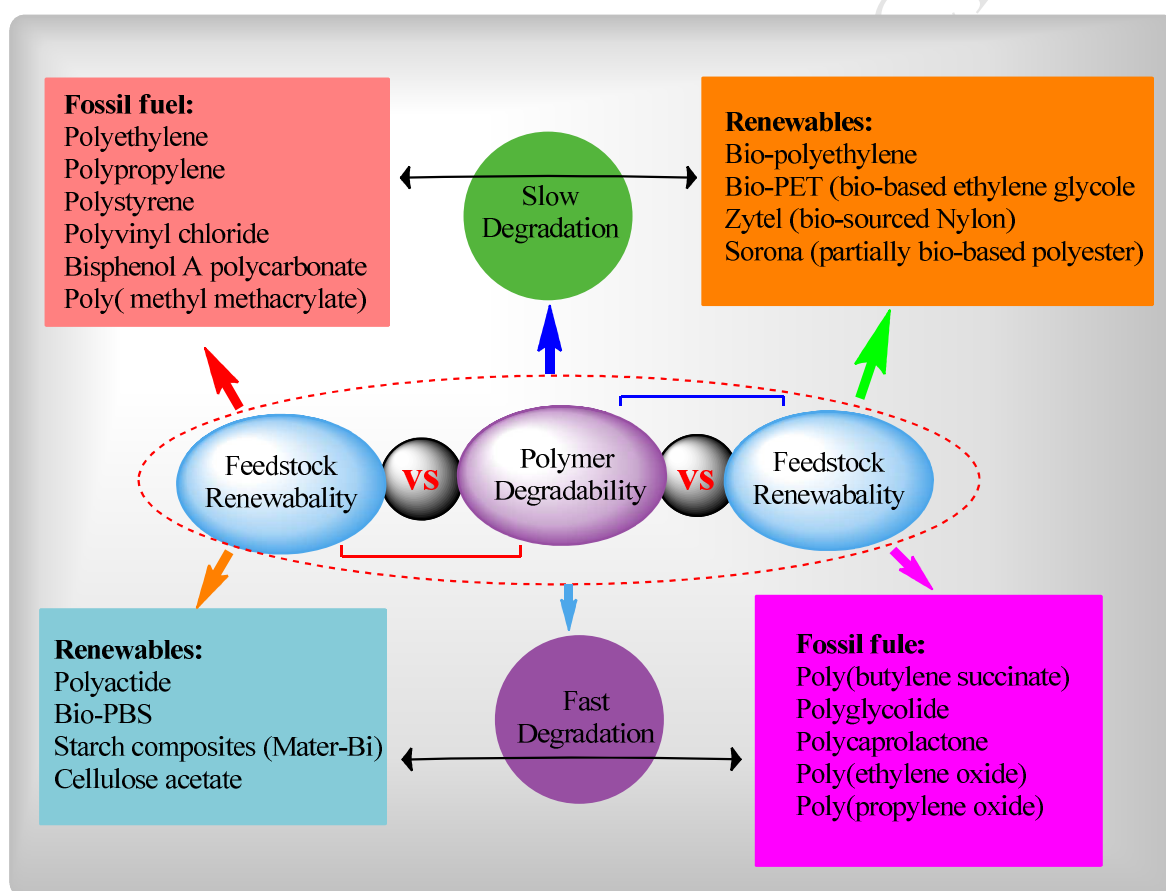


Figure 3. Polymer degradability and feedstock renewability of different polymers.

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Utilization of new generation bio-based plastic is beneficial but there is a need to analyze the negative environmental impacts [34]. These material showed high degradability in soil and compost systems but most of among these are not able to find a way in aquatic system [35]. Moreover, dumping of bio-based waste in landfills leads to global warming and leachate as well creates more management problems, so there is still a need to develop alternative techniques to attain sustainability.

Factors affecting the rate of degradation

Various factors have affected the rate of degradation of polymers. Mainly degradation of polymers depends on environmental factors (temperature, moisture, acidic nature etc.) and the chemical nature of the polymer [28]. Another factors that can affect the rate of degradation are crystallinity, molecular weight, co-polymer composition and size of the polymer [36,37].

Water and moisture can play an important role for bio-degradation of polymers, because water is a necessary condition for growth and reproduction of the microorganisms [38]. When moisture is growing, the microbial activity also increases and the polymers degrade with faster rate. Ho et al. reported that degradation rate sharply enhanced with increase in humidity [37]. Hence, the polymer will degrade rapidly in the moisture conditions than in dry conditions.

Acidic nature of the environment also affects the bio-degradation of the polymers. pH value changes the rate of hydrolysis reaction and growth of the microorganisms [38,39]. Temperature is an important factor for the degradation of polymers [40], degradation is not possible without required temperature. The rate of hydrolysis reaction and microbial activity rises with temperature but very high temperature reduces the microbial activity or even stops it [41]. Henton et al. described that the rate of hydrolysis reaction and bio-degradation of polymer

rapidly increased when the temperature exceeded the glass transition temperature [42]. Kai-Lai et al. studied the degradation rate of the polylactic acid film for different temperatures 28, 40 and 55 °C at 50 and 100% relative humidity in an environmental chamber [37,43]. Generally, the rate of microbial activity grows with temperature until it reaches the range when killing of the microorganisms starts to dominate.

Apart from the above mentioned factors, other factors of bio-degradation are the aerobic and anaerobic environment. Gertisar et al. performed anaerobic degradation tests for different available biodegradable polymers [44]. The flexibility of the polymer chain increases the biodegradability of polymer. If a polymer chain is more flexible, then hydrolysis reaction will proceed with higher speed and rate of bio-degradation also increases [36].

Another factor affecting the rate of bio-degradation is molecular weight of the polymer [45]. Larger will be the polymer molecular weight, lesser will be the flexibility of the polymer and greater will be the polymer's glass transition temperature [46]. Moreover, polymers with high molecular weight have less water solubility which reduces the microbial activity.

Co-polymer composition means the foreign co-monomer entering into the polymer structure, due to this reason, crystallinity decreases and biodegradability increases. Chiellini and Corti studied that bio-degradation rate sharply increased after adding the polycaprolactone (biodegradable ester) into the lignin [47]. At last, size and shape of the polymer also affect the rate of the bio-degradation [10,36,38,45,48]. If the size of the polymer is larger, biodegradability becomes very slow. On the other hand, polymer with larger surface area has high biodegradable rate as compared to polymer with smaller surface area [49]. International Standards Organization and American Society for Testing and Materials [50] require the control of size and shape of polymer before the bio-degradation test.

Biological recycling

Over the last decades, the process of biological recycling has given a new support to waste management. Use of plastic material is not sustainable. Moreover, due to its prolonged longevity, the amount of garbage is showing a solid edge in a landfill [51]. Biological recycling is a waste reduction strategy whose cornerstone are biological organisms. In sustainable recycling, first we have to degrade the material and then reuse it any positive direction. Accinelli et al. explored the use of recycled bioplastic granules for decreasing aflatoxicity in *Aspergillus flavus* [52]. The rate of decrease was more in low density recycled bioplastic in comparison to higher-density bioplastic.

Date back to the early 1960's, Merrick and Doudoroff first reported the microbial degradation of polyester [53]. Many focused studies have been performed to degrade aliphatic polyester and polycarbonate mainly by bacteria, enzyme yeast, fungi and cell extract in the labs or in the natural environment like in soil or in aqueous settings [54]. In addition to this, enzymes are the natural or synthetic biological catalysts which trigger the depolymerization of polymer, polycarbonate and aliphatic polyesters [55]. For example, proteases cleave the peptide bond in poly-L-lactic acid whereas, esterases hydrolysis the ester bonds of fats and depolymerizes the polyhydroxyalkanoates, poly-ether sulfones and poly-ester amide [56,57]. Basic mechanism of bio-degradation is the oxidation or hydrolysis by enzymes which eventually improves the hydrophilicity of plastic material, resulting in low molecular weight polymer which is more friendly for further microbial assimilation [58]. In case of enzyme hydrolysis, a bulk of metal is lost but no substantial change takes place in the molar mass that means the basic phenomena of biological degradation is the surface erosion [59]. However, if there is a decrease in the molar mass that means bulk erosion is taking place. Hence, to decrease the molecular mass of the

polymers, microbes first release the extracellular enzymes. **Figure 4** explains the working mechanism for bio-degradation of polyesters and polycarbonates through bacteria.

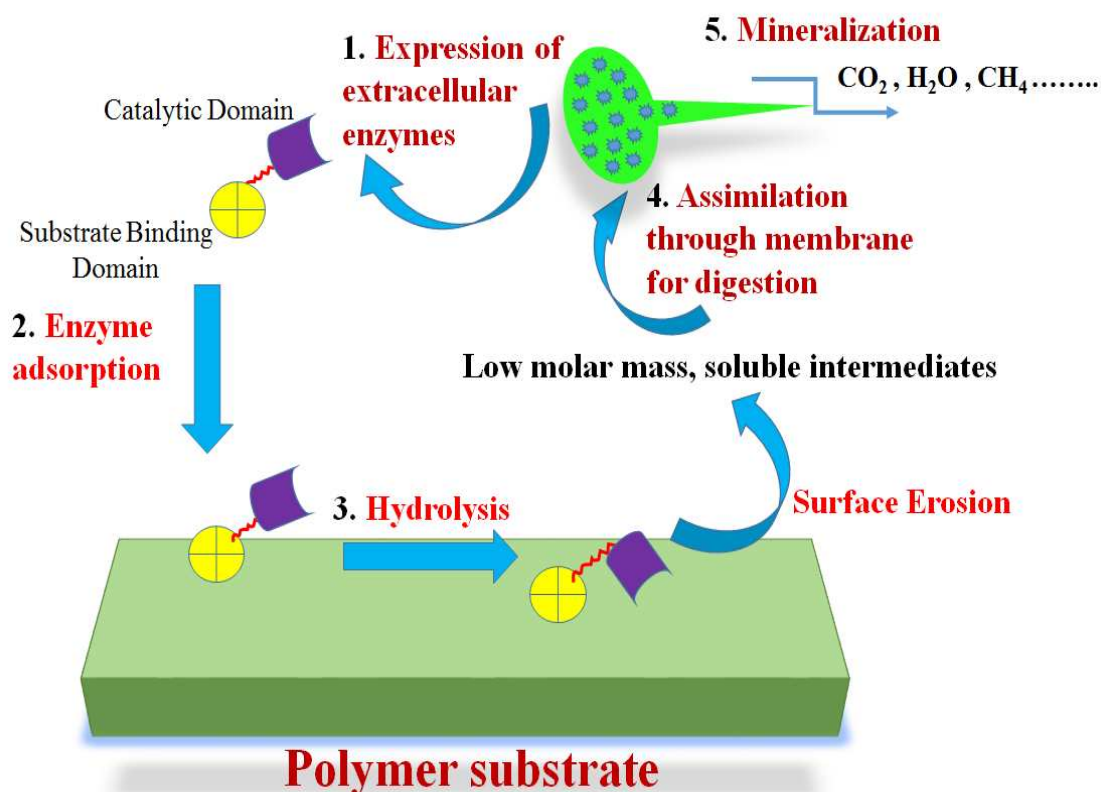


Figure 4. Water insoluble polymer bio-degradation through a bacterium. Reproduced with permission from [25]. Copyright 2017 American Chemical Society.

After degradation, fragmentation is the next considerable step to recycling [60]. The step is taken into account only when molecules are of low molecular weight within the media. It is a lytic phenomenon that undergoes breaking of a polymeric chain of plastic, which is necessary for assimilation of polymeric in the chain into the surroundings [61]. Importantly, the efficiency of bio-degradation can be analyzed from a number of tests, some of which are weight

measurements, qualification of evolved CO₂, analysis of the surface morphology of polymer after microbial degradation, these all measurements can be tested under anaerobic or aerobic conditions [62]. Rather than synthetic polymers, several oligomeric polymers can be degraded via biological method, for example, polyethylene degraded by two mechanisms: hydro-biodegradation and oxo-biodegradation [63].

Anaerobic bio-degradation by bacteria

Anaerobic conditions are mainly susceptible for the degradation of polylactide, phosphino-carboxylic acid and polyhydroxyalkanoates. The energy that comes after mineralization process is used by the microorganism and biomass [64]. Although biological energy comes to the oxidation process but in case of anaerobic organism, they use alternative electron acceptor like sulphate and nitrates to induce a change in the activity of microbial population [65]. Itavaara et al. have studied the degradation rate of polylactic acid and poly-L-lactic acid in aquatic condition degraded by soil bacteria [66]. They mentioned that polylactic acid degraded up to 90% after 55 to 60 days and poly-L-lactic acid degraded up to 50 % after 40 to 45 days. Rates of degradation in anaerobic condition are lower because in the absence of oxygen such type of microorganism has a limited enzyme population [67]. The bio-degradation rates for polylactic acid and polyhydroxybutyrate were much faster in anaerobic conditions rather than in aerobic conditions whereas poly(butylene succinate) was degraded slowly with only 2% of degradation rate in 100 days [67]. Johnson et al. evaluated the degradation effects of 11 types of starch-based polyethylene plastic collected from municipal waste by different degradation methods [68]. A very little degradation was found in interior plastics of compost row by 8-month, whereas exterior plastic degraded well.

Aerobic degradation by bacteria

During aerobic degradation by bacteria such organisms have the key to work with oxygen and mineralization, CO₂ and CH₄ are formed as the end product. Bio-degradation efficiency of aerobic bacteria is primarily influenced by the nature, origin and experimental conditions of labs [69]. It was reported that after isolation, the bacteria became more efficient in experimental conditions having low temperature and high pressure [70]. For example, isolated *Pseudomonas* and *Tenacibaculum* were partially able to mineralize the fibers of polycaprolactone and polyhydroxybutyrate [71]. Many standardized methods are used to determine the disintegration and degradation of plastic materials. Apart from them, a most common norm is the ISO 14855 (International Standards Organization). It is the ultimate method to measure biodegradability rate and degree of disintegration under the composting condition like controlled temperature, humidity and ventilation [72]. The degradability of poly lactic acid bottles in composting conditions was evaluated by Kale and co-workers [10]. Most of the polycarbonate and ester are degraded by enzymes, microbes etc. [73]. An extraordinary work of Lee et al. depicted that pure (R)-(-)-3-hydroxycarboxylic acids could be derived by depolymerising poly-3-hydroxybutyrate in presence of oxygen (aerobic) as well as in absence of oxygen in *Alcaligenes latus* [74].

Challenges and future prospective

Green Design Principle is a useful aspect for evaluation and its related activities on design to evaluate an environmental consequence of a product. In the design phase of sustainable polymer, Green Design Principle will be adopted as a preventive matrix to identify leverage points for the processes. It is based on green chemistry principles, which aims to reduce the utilization of toxic substances and production of chemical products in life cycle process. In the design phase of the durable polymer, green design theory can be adopted in the coming time. The circulation of

bioplastic is mainly subjected to the authenticity acquired by the new technology and the legitimacy of the companies who produce, sell and promote the sustainable technology [75]. Sustainability needs a communication with societies and markets about how bioplastics put in service in the future? How to get better bio-degradability? Affordable and convenient recycling plants? Better agricultural applications? [76]. Furthermore, the possibility of using more bioplastic materials can be further investigated to enhance the lifestyle of the community and reduction in recycling cost may open new horizon of applications in many fields like agriculture, medicine and many more because biodegradable polymeric materials are the strongest rivalry to beat petrochemical based plastic in the future [77].

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* of special interest

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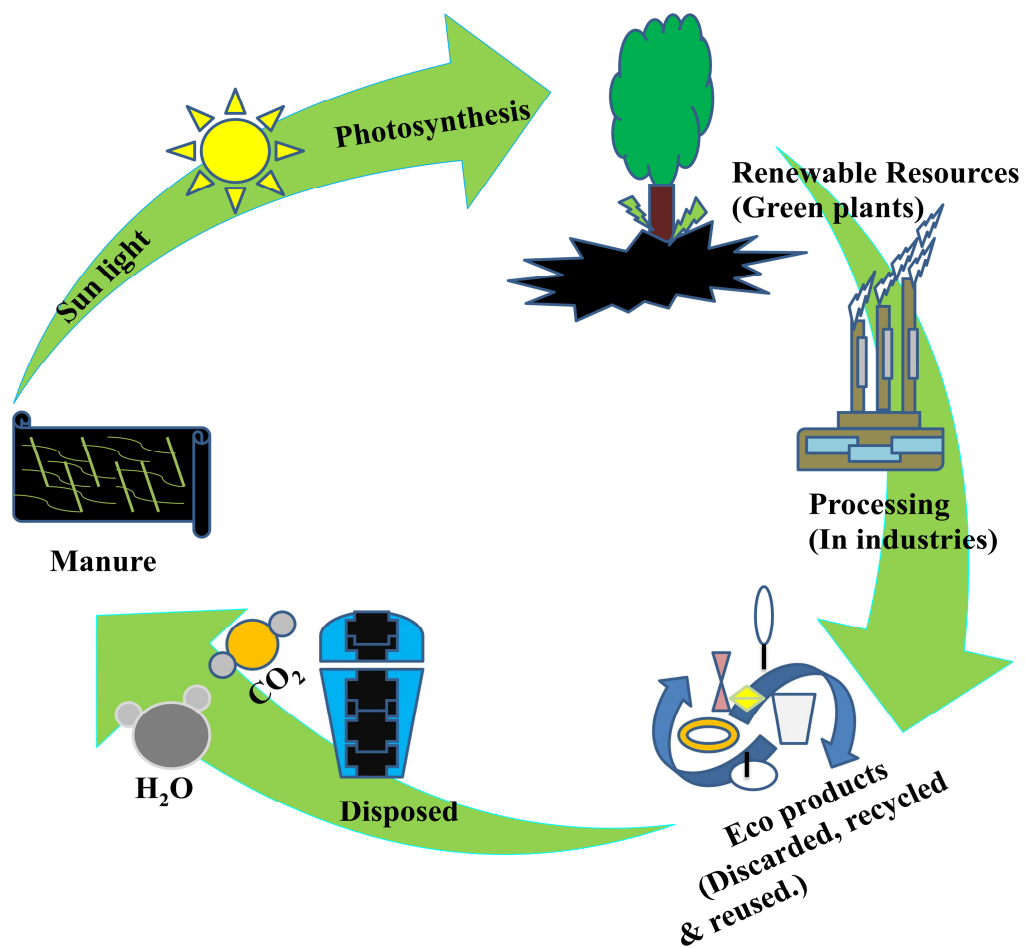
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Highlights

- The biological process of recycling has given a new direction for waste management.
- Bio-degradable plastic is useful in food packaging, shopping bags and agricultural applications.
- Sustainability needs a communication with societies and markets about how bio-plastics can be put in service in the future.

Graphical Abstract

Sustainability of bioplastics: opportunities and challenges

Thakur, Sourbh

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