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Exploring the Potential of Manufacturing Bioplastics from Waste and Wastewater Sources: A Review

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| Article Info. | Abstract |
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| <i>Article history:</i> Received 25 April 2025 Accepted 16 June 2025 Publishing 30 June 2025 | Plastic products are utilized as packaging materials with numerous features including durability, strength, and low density in comparison to paper and glass. However, the accumulation of plastic would be a considerable pollution issue negatively affecting the ecosystem. This is because of its high resistance to degradation. Several researchers endeavored to manage the accumulation of plastic by devising processes such as incineration, recycling, or reuse. However, the disposal of highly toxic compounds, including hydrocyanic and hydrochloric acids, during incineration is a main associated issue. Realizing these points, manufacturing bioplastics instead of using plastic oil appears to be a competent option. Specifically, polyhydroxyalkanoate (PHA) is a well-known type of bioplastic that can be manufactured via fermentation using bacteria. In this review, the main basics of bioplastics are presented outlining the aspects of biodegradation as a sustainable industrial process compared to plastic. Specifically, this review intends to shape the synthesis of PHA from waste and wastewater sources. This includes the review of PHA structures, properties, industrial methods, and an intensive review of the feast-famine mechanism. Lastly, a critical evaluation of this industry, along with challenges and suggestions for improvements, is addressed. |

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1. Introduction

Plastic pollution is a serious environmental concern, with millions of tons of plastic waste accumulating in landfills and oceans each year, thereby harming wildlife and ecosystems. Traditional plastics persist for centuries due to their durability, which can lead to significant ecological damage. Consequently, bioplastics such as polyhydroxyalkanoate (PHA) are a sustainable alternative, as they are derived from renewable biomass and can biodegrade extensively under specific conditions, mitigating their long-term environmental effects. The production of PHA from waste not only addresses plastic pollution but also contributes to waste management by converting potential pollutants into valuable products. However, a number of limitations, including economic feasibility, technological concerns, and scalability, should be addressed [1].

Generally, plastics are massively used worldwide due to their desirable characteristics, making them useful in many industries. Applications of plastics can be seen in agriculture, manufacturing, and services. Despite the benefits that plastics have, a big environmental issue is imposed which is white pollution [2].

The concept of white pollution is caused by the release of the following substances into the environment: non-biodegradable plastic, solid wastes, CO₂, toxic gases, hydrocarbons, dioxins, and aromatics [3,4]. Once these substances are released into the environment, their degradation takes a long time as it is very slow, especially when large quantities are released at once. Alcaraz Cercós [5] stated that due to the enormous usage of various types of plastics in almost all industries, waste accumulation and greenhouse gas emissions have become serious environmental problems. Thus, controlling such problems and reducing their negative impacts is compulsory. It is acknowledged that annually, approximately 7.8 to 8.2 million tons of mismanaged plastics enter the oceans [6].

One technique used to reduce environmental problems caused by plastics is recycling, which limits the quantity of plastics in waste [7]. However, the rate of elimination was inadequate for high-density recycled plastic compared to low-density recycled plastic. As a result, various studies have been carried out to discover eco-friendly options. An eco-friendly option is bioplastic, which can degrade much faster than typical plastics via the enzymatic actions of microorganisms [8, 9]. The significance of bioplastic lies in its ability to be not only environmentally friendly but also biocompatible with the human body [10].

| Nomenclature & Symbols | | | |
|------------------------|--|------|--------------------------|
| PHA | Polyhydroxyalkanoate | VFAs | Volatile Fatty Acids |
| ASTM | American Society for Testing and Materials | PLA | Polylactic Acid |
| ICI | Imperial Chemical Industries | MMCs | Mixed Microbial Cultures |

Interestingly, during biodegradation, CO₂ emissions are minimal, adding further advantages to manufacturing bioplastics [11]. Thus, bioplastics are becoming more preferable in industries as non-biodegradable plastics have caused significant environmental impacts [6].

Various forms of bioplastics are found; however, the most common one is PHA (Polyhydroxyalkanoate) [12]. This type is considered an energy storage substance for many microorganisms when nutrients are scarce.

In wastewater treatment plants, multiple pollutants, such as wastewater sludge and heavy metals, are present, which are difficult to treat [13–15]. At this moment, sludge management is the most challenging and biggest issue in wastewater treatment plants [16]. Methods like traditional stacking, incineration, and composting have disadvantages like reduced efficiency and high expense. According to several studies, PHAs were found to be present in sludge [5]. Specifically, biological treatment of wastewater usually includes a step where activated sludge can quickly transform degradable substrates into PHA instead of using them for growth and development [17]. Excess sludge can also be used to manufacture more PHA via a bacterial consortium and volatile fatty acids (VFAs) [18]. This way, a section of the issues regarding the disposal and manufacturing of municipal and industrial activated sludge, is reduced [19]. Hence, the expense of sludge treatment and disposal is lower (the most advantageous point). However, this procedure is mostly expensive [20]. Thus, various researchers worked on ascertaining the potential of manufacturing PHA from different resources, such as activated sludge as a mixed culture.

To produce PHA with reduced expenses, waste and wastewater are used as raw materials. This ensures a large quantity of PHA is produced and eliminates expenses for waste and wastewater treatment [4]. Thus, the activated sludge utilized in the studies of PHA synthesis was accustomed to using synthetic wastewater in a laboratory, while other researchers focused on the deployment of activated sludge sourced from full-scale wastewater treatment plants [21]. It is significant to realize that both the quantity and type of carbon source play a major role in PHA synthesis [22].

A few successful reviews can be found in the open literature that elucidates the production of PHA. For instance, Meereboer et al. [12] focused on revising the most recent advances in the biodegradability of PHA bioplastics and their composites as sustainable alternatives to traditional plastics. The researchers employed a comprehensive review to analyze the existing published studies on PHA production techniques, characteristics, and degradation mechanisms across different environments. The obtained results indicated that PHAs can demonstrate remarkable biodegradability in aerobic and anaerobic conditions, that are associated with the ASTM standards. However, PHAs are costlier to produce than petroleum-based plastics. The cost can be mitigated by blending natural fillers, which would also improve biodegradation. The review signified the potential of PHAs to mitigate plastic pollution and carbon emissions. Also, de Castro et al. [23] evaluated the potential of cleaner fermentation processes to produce bioplastics, particularly PHA and polylactic acid (PLA), as sustainable alternatives to synthetic plastics. The researchers introduced a narrative review of wide-ranging literature, concentrating on the environmental advantages, challenges, and sustainability of these bioplastics. The obtained results indicated that both PHA and PLA can be produced from renewable resources, which elucidated biodegradability, affording them promising for mitigating plastic pollution. The main limitations, including the high production cost and competition with food sources, were addressed in this review, which deters their widespread adoption.

The current study focuses on reviewing the biodegradation characteristics of PHA, its structure, and its physical and chemical properties. It also introduces the manufacturing steps of PHA from waste and wastewater resources, besides discussing the aspects of the feast-famine method and the influence of several parameters. The biggest challenges of PHA production and applications, along with suggesting affordable options for improvements, will also be outlined.

History of Manufacturing PHA: The production of PHAs originally started in the 1980s; however, they were rarely used due to the low cost of oil. In 2003, the cost of oil increased to more than US\$100 per barrel, which shed more light on the production of PHAs [24]. Since that time, petroleum-based oil products have not been sufficient to fulfill industries' demands. Hence, more plants were established in China, the USA, Italy, and Brazil [25].

In the UK, in 1976, a firm known as Imperial Chemical Industries (ICI) started exploring the properties of P₃HB that enable it to be generated economically via bacterial fermentation of carbohydrates. Wallen and Davis indicated the isolation of a bio-polyester in the 1980s, with physical characteristics close to P₃HB but having a diverse chemical structure. Due to the diversity of hydroxyalkanoic acid components, the biopolymers just like P₃HB were named polyhydroxyalkanoates (PHA) [5].

2. Biodegradation of PHA and the Influence of Essential Parameters

PHA indeed has close physical properties to plastics produced from petroleum i.e., polypropylene and polyethylene. However, PHA is outstanding due to its desirable features, such as being manufactured using renewable carbon, biodegradability, and biocompatibility (zero toxicity). As reminded by Harding et al. [26], such features enable PHA to be a great alternative to typical plastic. Biodegradation occurs in nature via microorganisms using PHA hydrolases and PHA depolymerases. PHA is converted into water carbon dioxide in aerobic conditions and methane in anaerobic, with no toxic products [27]. This points out that PHAs have no contribution to global warming (sustainable process) [28]. Another useful property of PHA is that it is biocompatible, indicating zero toxic impacts in living organisms [29].

Typically, predicting the rate of PHA's degradation is difficult and mostly affected by environmental factors, including temperature, pH, and oxygen content, as well as chemical structure, polymer chains, functional groups, the crystallinity of biopolymers (amorphous region rates), size of the polymer, polymer composition, and molecular weight [30, 31]. pH alters both hydrolysis rates and the growth of microorganisms. High temperatures enable improved degradation mainly because of elevated microbial activity. Rates of hydrolysis and microbial activity increase with temperature. The more flexible a polymer chain is, the more biodegradable it is. In this case, hydrolysis is faster hence faster biodegradation. Also, higher crystallinity means reduced biodegradation. A polymer with high molecular weight has lower flexibility and a

greater glass transition temperature. Likewise, they have both lower water solubility and microbial activity. Thus, low molecular weight polymers degrade faster.

The size and shape of the polymer play a role in the biodegradation rate. Larger polymer means slow biodegradability. Nonetheless, a polymer with a large surface area has high biodegradability in comparison to a polymer with a smaller surface area [32]. Finally, in the presence of moisture, both microbial activity and polymer degradation increase [33].

2.1. PHA: Molecular structure

As stated by Steinbüchel and Fuchtenbusch [34], PHAs are the most suitable biodegradable polymers, having features close to typical plastics. The accumulation of bacteria into linear polyesters as a source of carbon and energy results in the production of PHA. When comparing different groups of biopolymers that have similar characteristics to plastics, it was found that PHA is solely manufactured and degraded via living cells [5]. The conditions under which they were produced are extensive, i.e., supplies of nitrogen, phosphorus, or oxygen limitation with excess carbon sources.

Once carbon substrates are regulated, the structure of PHA is easily controlled in gaining desirable monomers. This procedure occurs either by designing metabolic routes on the hosts or by supplying the culture with carbon substrates containing functional side chains, where chemical alterations would occur later [35].

Fig. 1 shows the structure of PHA, which signifies three different associated R groups within the PHA structure as given in Table 1. Typically, shown in Fig. 1, varies between 100 to 30,000 and depends on the type of both microorganisms and pendant group [36]. It is said that distinguished types of PHA are generated by bacteria depending on the hydrocarbon chain length between the carboxyl group and the side chain R, and the side chain length as well [37]. Fig. 2 depicts the general structure of PHA that consists of alkyl groups of R1 and R2 between C1 and C13, respectively.

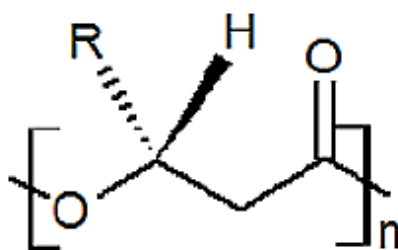


Fig. 1. Structure of PHA [38]

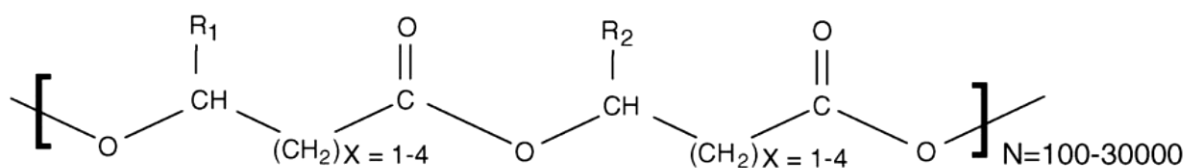


Fig. 2. Typical structure of PHA with R1 and R2 of alkyl groups (C1–C13) [39]

Table 1. General associated R groups within PHA

| Name | R group | Abbreviated name |
|--------------------------|---|--------------------|
| Poly(3-hydroxybutyrate) | CH ₃ | P ₃ HB |
| Poly(3-hydroxyvalerate) | CH ₂ CH ₂ CH ₃ | P ₃ HV |
| Poly(3-hydroxyhexanoate) | CH ₂ CH ₃ | P ₃ HHx |

The monomer composition of PHA impacts its physical properties, and therefore it is important to understand the three different classification groups of PHA in terms of their monomeric structure. These classifications depend on the chain length of the fatty hydroxyalkanoates [40]. Those include long (PHALCL), medium (PHAMCL), and short (PHASCL) chain lengths hydroxyalkanoic of fatty acids of more than 14, 6-14, and 3-5 carbon atoms, respectively.

2.2. PHA: Physical and chemical properties

Both PHAs and their copolymers are known to have low crystallinity, from 20 to 40%, and do not break easily [41]. In terms of PHA's mechanical properties, they are in direct correlation with both structure and crystallinity. For PHAMCL, when various side chains are present inside a polymer, the polymer's ability to crystallize would be altered. Hence, PHAMCL has different crystallisation features depending on the side chains. At typical conditions, when there are large and irregular side chains, crystallinity is low. However, it should be noted that several factors like monomer composition, molecular structure and chemical or physical characteristics of PHAs differ as they rely on both producer organisms and carbon sources for growth [42].

Conditions of manufacturing and recovery of compounds affect the molecular weight of PHAs [38]. Usually, bacteria used in PHA manufacturing produce an average molecular mass (Mn) of 4.0×10^6 Da. When organic solvents are used for extraction purposes, polymers with higher molecular weights are generated [43]. However, when sodium hypochlorite or other various chemicals are used, the molecular weights are lower. Hence, a variety of PHAs can be found with different molecular weights varying between 56,000 to 1,400,000 [5].

2.3. Description of PHA manufacturing from waste and wastewater sources

The first time PHA was synthesized using mixed cultures was in wastewater treatment plants mainly for biological phosphorus removal, where alternating anaerobic and aerobic stages would occur. PHA production from waste and wastewater is an example of a technology known as mixed microbial cultures (MMCs), utilized in the field of practical microbiology and bioprocessing engineering [44]. Many species of microorganisms are responsible for the production of biopolymers that function as intracellular carbon and energy sources.

The production of PHA using waste or wastewater resources involves three stages: acidogenic fermentation, selection of the culture and lastly accumulation of PHA [45]. In fermentation, fatty acids are produced when the substrate is a carbohydrate waste. Particularly, the organic content is converted into VFAs. For the last two stages, the feast-famine technique is used to limit organic loads. The major struggle found in the PHA mixed culture method is the reinforcement of PHA-accumulating organisms, which happen under temporary conditions of carbon supply. However, it is necessary to physically segregate culture selection and PHA production due to the varying conditions needed for each stage. Culture selection plays a role in affecting mixed microbial cultures of PHA production via the bioreactor conditions. Several examples of MMC-PHA production can be found in open literature. For instance, several laboratories to pilot scale facilities were developed via the integration of MMC-PHA with municipal wastewater treatment, food and dairy-processing wastewater, and excess sludge fermentation liquid [46]. The three synthesis pathways in the system of both wastewater biological treatment and PHA accumulation recovery (MMC-PHA) are schematically shown in Fig. 3, which uses polyphosphate accumulating organisms and glycogen-accumulating organisms. The benefit is the simultaneous procedure of PHA production and phosphorus removal from wastewater. However, the drawback is a low and unstable PHA production level [21].

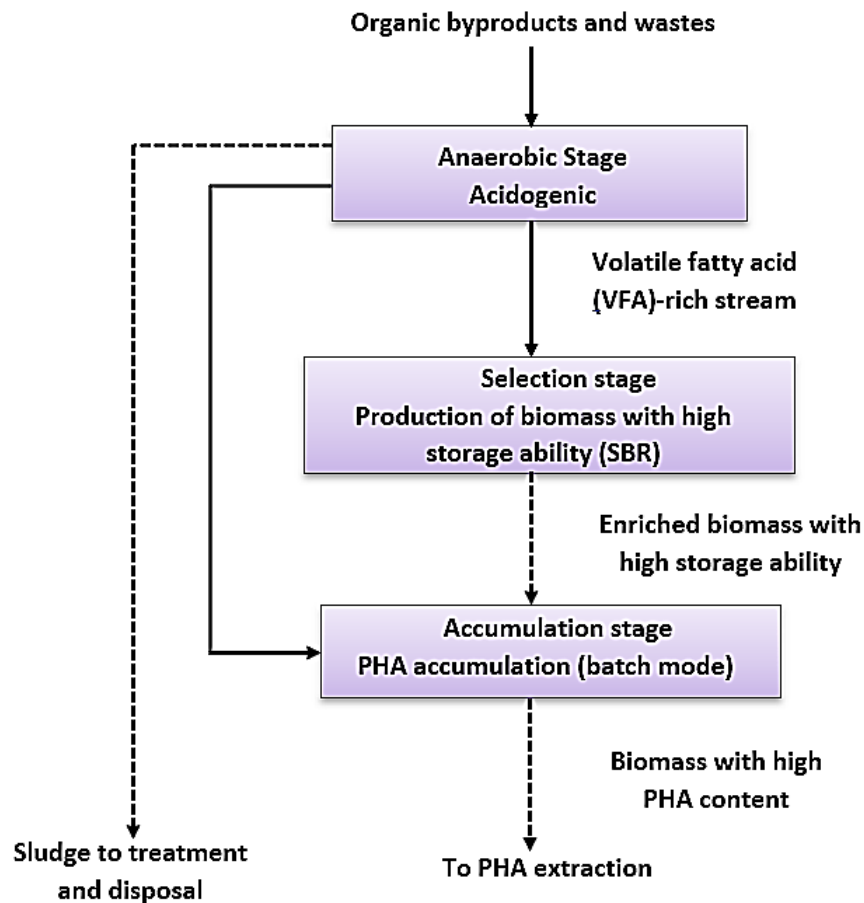


Fig. 3. Three-stage industrial method of MMC-PHA production from waste and wastewater (Adapted from [47])

For large industrial-scale PHA production, both batch and fed-batch fermentation processes take place. Batch fermentation is usually flexible and has low operational expenses. However, the bacterial degradation of the accumulated PHA leads to low PHA production levels. For fed-batch, it is considered more effective as both high-production rate and cell concentration are achieved. Therefore, to ensure maximum production level, batch and fed-batch are combined. The combined procedure is becoming more popular for PHA production where two stages are involved [47]. This is known as the feast-famine process, where PHA is accumulated for storage as cells become bigger in both size and weight [5]. Once the feast-famine mechanism begins, microorganisms face major alterations in their internal metabolism to adjust to the environment. These microorganisms can store PHA efficiently and have strong and consistent PHA accumulation levels [21]. More details of the feast-famine method are illustrated in the next section.

3. Feast-Famine Mechanism

The feast-famine mechanism of PHA manufacturing from waste and wastewater sources is initiated with fermentation in three stages, including producing VFA-rich concentrate in the 1st stage, manufacturing biomass by treating waste in the 2nd stage, and lastly manufacturing PHA in

the 3rd stage using the surplus biomass from the 2nd stage and concentrate from the 1st stage (Fig. 4). The 1st step is called acidogenic fermentation, where anaerobic digestion of organic compounds to CH₄ and CO₂ occurs. The fermentation of soluble organic compounds produces several organic acids and other fermentation products [47].

Throughout this operation, a control system is used to ensure the temperature stays constant, and a downstream centrifugation unit and a stirred tank ensure the solids are segregated. The untreated feedstock is waste-activated sludge [48]. A batch mode is used where an inherent buffering is ensured. pH levels are between 5.5 and 6.5 [49]. The optimum temperature was determined to be 42 °C with batch-fermentation times of 4-5 days to result in a concentrate as a feedstock for 3rd stage. To ensure nitrogen supply is limited, the COD:N mass ratio should be 300:1. From the centrifuge unit, VFA is used as a feedstock for 3rd stage [50].

2nd stage of fermentation occurs in an SBR feast-famine scheme. As stated by Morgan-Sagastume et al. [16], a wastewater supply line and a micro-filter are used for solid eradication. A feed-holding tank is used for wastewater treatment, and lastly, a batch reactor and an aerated tank ensure active biomass storage (Fig. 4). The feedstock for this stage is wastewater influent after inspecting soluble and insoluble materials removal [51].

Both the wastewater supply line and filter must be maintained to guarantee a decent feed for the 2nd stage. Using SBR in this stage is intended to stimulate an ideal continuous flow process with a fixed volume of short aerobic plug-flow. This would be pursued by solids segregation, and a famine unit for the arrival of activated sludge biomass (Fig. 4). An aeration of the biomass storage tank is essential to ensure sufficient oxygen in the process. Furthermore, the selection of an appropriate culture stage is significant for PHA accumulation in the subsequent production step [5].

In the 3rd stage, the biomass is obtained from the 2nd stage when it was fed with concentration from the 1st stage to ensure the highest storage volume of MMC-PHA. In this stage, an accumulation reactor, a dewatering centrifuge, a dry oven, and a downstream active biomass unit are included (Fig. 4) [16]. In addition, recycling of the accumulation reactor takes place, where a stream from the reactor reaches the settling tank. This segregates the effluent from the central stream, which accumulates in the reactor once more [16].

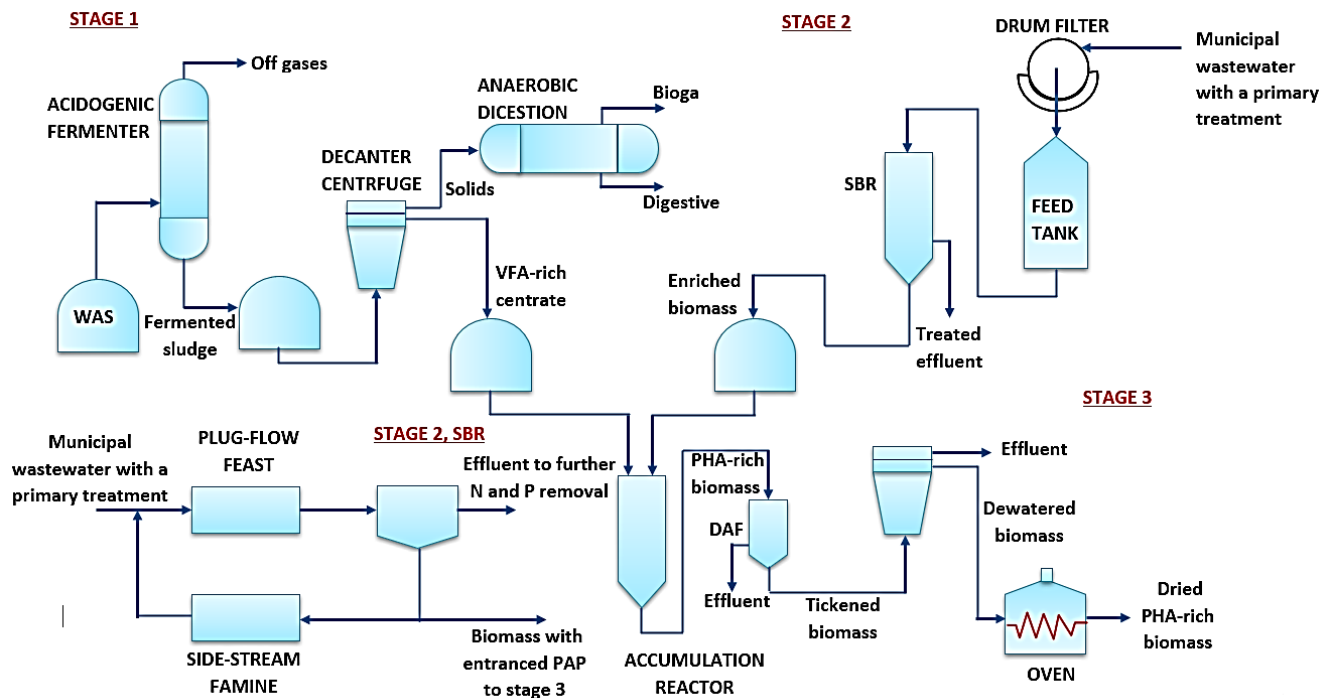


Fig. 4. Stages of feast-famine method of PHA production (Adapted from Morgan-Sagastume et al. [16])

4. PHA Extraction and Purification Stage

Once fermentation is completed, bacterial cells having PHA are segregated from the medium via centrifugation. The technique used for reliable segregation of PHA from biomass is expensive and complicated. Chloroform is the technique used for PHA extraction from biomass via solvent extraction [52]. Filtration of the PHA solution occurs to remove cell debris before placing PHA in either methanol or ethanol. This technique ensures that PHA with high-purity levels is obtained without any PHA degradation required [5].

Continuous centrifugal fractionation results in 85% of PHA having a purity of more than 95%. The recovery of PHA using crops via air classification involves segregating finely ground solid elements based on either weight or size. The terminal parts have greater PHA concentration which can be recovered via filtration and centrifugation. Here, 90% of PHA with a purity range between 85 to 95% is obtained [52].

5. Challenges of PHA Production

Despite the advantages of bioplastics and specifically PHA, below are the associated challenges with PHA production from waste and wastewater sources.

- High expense: Currently, bioplastic expenses are greater than three times typical plastics as they are rarely used. Its production is limited to small quantities due to this reason. Once production expenses are reduced, production is expected to increase. For large-scale production, decreasing the cost relies on total process optimization [53].
- Shortage of known bioplastic labelling procedure: People have little awareness regarding bioplastic waste. The bioplastic industry is recommended to set out rules for bioplastic product labelling for easier comprehension and usage.
- The end-of-life management for bioplastic: No particular technique for assembling and treating bioplastic waste has been established, which inhibits bioplastic development.
- Toxicity: In case of wastewater sludge being used, non-metal oxides and heavy metals could be found in the produced bioplastic throughout the extraction stage. Hence, to reduce this effect, any toxic substances should be removed [21].
- Other challenges include difficulties in managing PHA structures and properties, extraction of PHA via current downstream units, and a shortage of high-value applications [54].

6. Criticize PHA Synthesis and Possible Improvements

Despite the advantages of PHA synthesis from wastewater, there are a few necessary points to be noted.

- Reducing expenses is important and thus requires a higher-efficiency fermentation process to improve recovery and purification.
- The presence of nutrients in production should be considered, as their shortage is not always desirable, particularly for large-scale production.
- The overall process of converting waste to biopolymers requires the cooperation of various participants including waste generation, collection, conversion, synthesis, and distribution of terminal product. For instance, a primary process generates waste whose quantity and properties may vary for the subsequent process. Hence, ensuring different areas of industry cooperate to achieve a smooth process is compulsory.
- Ensuring that waste produced from various industries is used in PHA production facilitates the recycling of resources. Controlling the overall substance flow is needed in terms of nutrients, contaminant accumulation, and waste conversion issues.
- In the feast-famine method of PHA production, the major goal is to have a highly stable PHA storage capability. Any microorganisms with low storage capabilities are undesired as they negatively impact accumulation during downstream processing, hence increasing PHA extraction expenses.

Based on the author's knowledge, there are several improvements that can be made to gain high-performance PHA production as listed below.

- Despite many factors affecting PHA production via waste, the downstream procedure is the major one. This stage can be optimized by improving the PHA content in the biomass and decreasing the use of chemical products. Both cyclic pattern and lack of VFA would offer a benefit for PHA storage species.
- Throughout the synthesis of PHA, choosing a decent carbon substrate is vital in influencing the performance of bacterial fermentation and expenses. Thus, choosing a renewable, low-cost, and available carbon substrate ensures good microbial growth and effective PHA production. In this regard, it is plausible to examine waste released into the environment due to agricultural and food processing, which can be used as renewable feed for PHA manufacturing, thus lowering PHA production and wastewater treatment expenses.
- In some cases, a pre-treatment is required for the waste stream for microbial PHA-producers. Choosing a waste stream relies on the production plant construction district.
- According to Bengtsson et al. [22], limited nutrients cause greater PHA content and yield by hindering cell multiplication. However, cell size and weight increase when PHA is accumulated for storage. Thus, it is important to reduce the nutrient content as much as possible to prevent cell growth.

7. Conclusion

Having high functionality with low environmental impacts is the selected polymer production substance named PHA. Such biopolymers are desired as their properties are close to typical plastics. The production procedure is managed by substrate selection, type of bacteria and fermentation conditions. Three stages are involved in PHA production: acidogenic fermentation producing VFA, feast-famine enrichment of biomass and lastly accumulation of PHA.

It is fair to admit that using waste for PHA production indicates a pre-treatment of this waste. Using sludge to synthesize PHA adds value to waste as bioplastic production expenses will be lower, ensuring efficient handling and recycling of sludge. When sewage is biologically treated to produce PHA, an enhanced biological phosphorus removal system and feast-famine mechanism both play major roles. However, at some points these two techniques do not meet the target thus, using a combination of the two leads to higher efficiency where greater quantities of PHAs are produced.

Undoubtedly, understanding the mechanism behind the different molecular weights of PHA produced by bacteria is yet incomplete. Nonetheless, it is expected that the type of bacteria or microorganism and the recovery technique of the polymer used affect molecular weight. Furthermore, the assortment of suitable carbon substrates is important to control the performance of the bacterial fermentation besides affecting the overall cost. The selection of renewable, inexpensive carbon substrates would be a feasible option to maintain a cost-effective PHA production. Nevertheless, the high expense of this procedure is a struggle for today's industries. Thus, more efforts need to be made to study PHA recovery expenses in terms of extraction and purification, as both processes increase the overall cost. Also, the concept of 'Zero Emission' in PHA synthesis is crucial for general sustainability to develop a highly efficient economical procedure for PHA production, isolation, and

purification. These would reflect the most important recommendations for the next research. Overall, investment in research and supportive policies is imperative to simplify the adoption of bioplastics, eventually contributing to a circular economy and a healthier planet.

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