Bioplastic production from wastewater sludge and application

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Abstract. Plastic is considered as one of the most useful materials in the world. Plastic products are utilized in almost any field such as industry, manufacturing, agriculture, and service. Although plastic products can meet the needs of human beings, they also cause environmental problems such as white pollution. The current utilized plastic is non-biodegraded. It suggests that they would remain in long time in the environment when they are Activated sludge (sludge is called for short) is generated during the wastewater treatment process in large quantity. Its management gradually becomes a great problem. The problem of difficult recycling of plastic waste has attracted more and more attention. Recycling technology is an effective but incomplete measure to address these environmental issues. Based on this, bioplastics can solve this problem as a new material. Studies have found that high temperature lysates of sludge can be used to produce biodegradable plastic poly-3-hydroxybutyrate (PHB). And acetic acid produced by the anaerobic fermentation sludge thermal cracking solution can replace glucose as a carbon source to support the growth of microorganisms. In this way, the use of sludge thermal cracking fluid to produce bioplastic PHB can be achieved. In this paper, the development of bioplastics is introduced in the context of understanding the development of bioplastics. This paper also introduces the various types of bioplastics widely used at present, discusses the principle of producing bioplastics from activated sludge, and prospects the application prospects of bioplastics.

1. Introduction

Synthetic plastics are organic polymers synthesized from monomers derived from the petroleum industry. In 1909, American Becker produced the first synthetic plastic-phenolic resin. Synthetic plastics mainly include polypropylene (PP), polyethylene (PE), polystyrene (PS), etc. Plastic has the characteristics of excellent comprehensive performance, low price, easy molding and processing, etc. Plastics have been widely used in various fields of the national economy and human life such as food packaging, electrical insulation materials, reinforced matrix and so on [1–4]. Plastic has been named as “Four basic materials” along with steel, wood, and cement. Plastic is not only the major support materials utilizing to make up the deficiencies in the quality and quantity of the traditional materials, but also an indispensable material for technical progress in some fields. About 4% of the annual oil production was directly used in the formation of plastic [5,6]. A large quantity of synthetic plastic wastes such as plastic mulch, shopping bags, cutlery, and packaging materials are normally directly disposed to the environment after utilization. The total amount of plastic waste is as high as 50 million tons per year in the world. Thus, serious problems in farmland, tourist resorts, coastal ports, and animals (birds, fishes, big wild animals) have been caused. Moreover, the raw material (petroleum)
used to prepare plastics is getting declined.

Bioplastic is a type of plastic made from biomass materials. Biomass normally refers to a union of microorganisms, which mainly contains macromolecules including starch, cellulose, protein, etc. The biodegradability of bioplastic has become an important feature for its application. In addition, bioplastic is not only environmentally friendly, but also adaptable to the human body. Therefore, bioplastic is expected to be used in the production of medical products (such as postoperative sutures) [7]. Due to these advantages of bioplastic, researchers and engineers try to promote its production and application. Nowadays, the main obstacle to the growth of the bioplastic market is its high production cost. Bioplastic products are still rare and struggling to gain a massive production [8]. Economic evaluation shows that if the production cost of bioplastic can be reduced more than 50% if activated sludge were used to generate PHA [9]. Hence, the key point is to reducing cost.

During the treatment of wastewater, there are many pollutants including heavy metals and wastewater sludge which is hard to handle. Researchers synthesized polyaniline Sn (IV) silicate composite cation exchange material with good ion exchange capacity and high selectivity for heavy toxic metal ions [10]. They also did research on how to remove other metal ions (Cd (II), Co (II), Cu (II), Pb (II) and Hg (II)) using composite cation exchanger [11-13]; study the adsorption of Hg$^{2+}$ from aqueous medium using alizarin red-S-loaded amberlite IRA-400 resin [14] or Surfactant assisted nano-composite cation exchanger [15]. Currently, sludge management is the most difficult and largest problem in wastewater treatment plants. Traditional stacking, incineration, and composting have some problems such as low efficiency and high cost. Studies have revealed that sludge contains Polyhydroxyalkanoates (PHAs) component [16]. PHA can be produced by a bacterial consortium and volatile fatty acids (VFAs) generated from excess sludge [17,18].

Utilization of sludge for the PHAs production could turn waste into value-added products. Thereafter, the bioplastic production cost will be reduced and the sludge will be treated and recycled.

The following aspects, including the concept of bioplastic, the pathway of bioplastic formation from wastewater sludge, and the future of bioplastic, are reviewed.

2. Bioplastic

Bioplastic can be produced through two methods. One way is from biosynthesis of microorganism as an energy storage component such as polyhydroxyalkanoates (PHA). The other way is from the chemical formation such as (poly (p-phenylene) formic acid diol ester (PTT) and polyactic acid (PLA). The former way is more attractive as it is more environmentally friendly compared to the later one.

Currently, the bioplastic is divided into all-bioplastic and part-bioplastic. All-bioplastics are the ones which are all derived from biomass materials. The others are part-bioplastics.

Part-bioplastics mainly contain starch bioplastic, the bioplastic modified with natural biomaterials like starch and cellulose by using FTIR and SEM such as PSM (resin or starch composite plastic), PTT (poly (p-phenylene) formic acid diol eater) plastics [19], in which propylene glycol synthetic monomers are derived from biomass materials, plastic-wood products, plastic-wood products obtained by blending biomass materials with petroleum-based plastics, which is mainly based on PE (polyethylene) and PVC(Polyvinylchloride).

All-bioplastics include protein plastics, such as soybean fiber, cellulotic, a cellulose derivative obtained by chemical treatment of natural cellulotic materials, algae-based resin, a California company announced the launch of a series of bioplastic resins based on all-natural algae that can be mixed with polypropylene or other resins for injection molding or thermoforming [20]. Cellulosicare the earliest type of modified plastic, such as nitrocellulose, cellulose acetate, etc. and still widely used for the production of eyeglasses, table tennis and film and so on.

Bioplastics can also be classified into biodegradable bioplastics and non-biodegradable bioplastics according to their nature properties.

Biodegradable bioplastic is a natural polymer modified class (PSM). Currently, it refers to industrialized starch/polymer blends and soybean protein full-degradable plastics. In fact, the cost of
starch/polymer blend materials is lower than that of ordinary polyethylene (PE) and Polylpropylene (PP). Its disadvantage is poor water and moisture resistance. The PHA, including PHB (poly 3-hydroxybutyrate), PHBV (3-hydroxybutyrate and 3-hydroxyvalerate), PBHH (blending of 3-hydroxybutyric acid and 3-Copolymerization of hydroxycaproic acid), P34HB (3-hydroxybutyric acid and 4-hydroxybutyric acid copolymer), is a typical biodegradable plastic, with all good features. However, the cost of PHA is high which is mainly contributing to the raw material.

3. **The mechanism of bioplastic synthesis with sludge**

Thanks to the fact that the PHA storage process is the quickest adaptation process for microorganisms tackling substrate (matrix) changes. In the biological treatment of wastewater, activated sludge can often rapidly convert readily degradable substrates to PHA rather than preferentially use them for growth and development [21]. PHA is a kind of granular internal storage that can be used as an intracellular carbon source and energy source of microorganisms to acclimate to the environment (such as high temperature, dryness, \( \text{H}_2\text{O}_2 \), UV radiation and osmotic pressure).

Due to the diversity of wastewater biological treatment process and the complexity of the community structure in activated sludge, the activated sludge systems has different PHA anabolic mechanism. Among all, two are the most important mechanism [22]: the Enhanced Biological Phosphorus Removal (EBPR) system and the dynamic substrate dosing mode, which is also called the aerobic dynamic feeding mode (Feast-Famine mechanism).

The content and composition of PHA in activated sludge are mainly related to the community preference to the substrate species and concentration of activated sludge. Organic acids with even number of carbon atoms such as acetate and butyrate (mainly synthesize hydroxybutyric acid (HB) monomers), and organic acids with odd number of carbon atoms such as propionate and valerate (mainly synthesize hydrovaleric acid (HV) monomers) can be used as substrates. In the actual domestic sewage, the content of acetate and propionate is high. Hence, PHA is mainly in the form of PHB and PHV.

3.1. **PHA anabolic pathway based on EBPR process**

The first way of the metabolic mechanism of PHA synthesis is based on EBPR (Enhanced Biological Phosphorus Removal) process. The synthesis pathway was schematically shown in figure 1 [23], which mainly utilizes the dominant populations of Polyphosphate Accumulating Organisms (PAOs) and Glycogen-accumulating organism (GAOs) in the system for wastewater biological treatment and PHA accumulation recovery. The advantage is the simultaneously PHA production and phosphorus removal from wastewater. The disadvantages are that PHA production is low and unstable.

![Figure 1. PHA anabolic pathway based on EBPR process [23].](image)

*Note: M\(^+\) is metal ions such as K\(^-\) and Na\(^-\).*
3.2. PHA anabolic pathway based on feast-famine mechanism
The second way for the metabolic mechanism of PHA synthesis by activated sludge process is based on Feast-Famine mechanism (figure 2). The mechanism is to accumulate PHA using activated sludge (microorganisms) by applying selective pressure to the system, which is to quickly add the substrate to the reactor, and then forms the so-called “Feast” (satisfaction) and “Famine” (hungry) alternative ecological environment. During the Feast-Famine, microorganisms undergo significant changes in its internal metabolism to adapt to the environment, and it becomes domesticated and enriched with dominant strains that have stored PHA function. The ability of this mechanism to accumulate PHA is strong and stable, which is currently the newest technologies with popularity, prospect and engineering application possibility.

![Figure 2. PHA anabolic pathway based on Feast-Famine mechanism [23].](image)

Note: P (3HB)$_n$ and P (3HB)$_{n+1}$ are 3-hydroxybutyrate ethyl ester polymers

3.3. Application of the above two mechanisms
Based on the above methods, it was found that a higher efficiency of PHA synthesis might be achieved by their combination [24]. Some researchers came up with the Three-stage Activated Sludge Process for PHA synthesis. In the process, the anaerobic reaction tank, activated sludge wastewater treatment process and batch reactor were used as the first, second and third stages, respectively. The first stage is to convert organics to VFAs via acidogenic fermentation. The second stage is to select and enrich acid-producing microorganisms. The last stage is to accumulate PHA. Experiments have shown that more PHA was produced [25,26].

4. The application of bioplastic
At present, bioplastic is mainly employed in five industries:
- Packaging industry
  Plastic packaging products are an important industrial chain in the plastic industry. Plastic can generally be utilized to produce shopping bags, trash bags, bottles, labels, packaging films, cushioning packaging materials, etc. Bioplastic can be used to produce these products instead of normal plastics.
- Textile industry
  The fiber made from bioplastic has better feel and breathability than common polyester, which can change the disadvantages of static electricity and poor air permeability of polyester material.
- Manufacturing industry
Bioplastic can be used to make children’s toys and home interiors, etc. Children always take toys as snacks; however, chemical plastics are toxic. Bioplastic is much safer than the general bioplastic.

- Medical industry
  At present, bioplastic is used in the medical industry mainly for medical bone nails and tissue scaffolds to avoid multiple patient surgeries, which is convenient and acceptable [27].

- Bioplastic agricultural film
  The original agricultural cover film is generally non-degradable plastic. It causes white pollution. The bioplastic film can be directly land-filled and degraded after being used, thus avoiding possible pollution caused by chemical plastics.

5. The advantages of bioplastic and the problem of its production

5.1. The advantages of bioplastic
As a new type of material, bioplastic can be recycled. The advantages of bioplastic have been recognized by the European bioplastic Industry Association. Its advantages are roughly divided into the following four points:

- Energy saving
  Plastics are prepared from petroleum industry, but the resource of petroleum is gradually decreasing. Using bioplastics instead of plastics could reduce the consumption of oil. During wastewater treatment, biomass is generated. As the source of bioplastic, biomass is inexhaustible. It is an abundant resource which is not well managed. Using sludge for PHA production seems to be an effective strategy in terms of sustainable development [28].

- Biodegradability
  Mostly, bioplastic has good degradation properties. In the environment, bioplastic could be completely broken down into water and carbon dioxide [29]. A number of microorganisms (such as bacteria and fungi in soil, sludge, and sea) excrete extracellular PHA degrading enzymes to hydrolyze solid PHA into water-soluble oligomers and monomers, and then utilize the resulting products as nutrients. The hydrolytic and enzymatic degradation processes of P (3HB-co-4HB) films were studied by monitoring the time-dependent changes in molecular weights and weight loss. The P (3HB-co-4HB) films were hydrolyzed by both PHA depolymerase and lipase [30-32]. Therefore, the application of bioplastic does not produce white pollution after disposal, because it can be landfilled and in situ biodegraded.

- Low carbon emissions
  The biomass formation needs to absorb a large amount of carbon dioxide during the growth process, it has the ability of carbon neutral. The carbon dioxide emission of bioplastic is equivalent to only 20% of petrochemical plastic. Therefore, bioplastic is also called low-carbon plastic. Utilization of the low-carbon plastic helps to control the elevation of temperature in Earth [33].

- Nontoxic substance
  The raw materials of bioplastic such as starch, cellulose and protein, which are all biomass based. Those materials do not contain any organic toxic substances [7]. Furthermore, bioplastics can be completely degraded into water and carbon dioxide which are also non-toxic [29].

5.2. The problems and challenges of bioplastic
Bioplastic is a new type of material. It is considered as a promising replacement of plastic due to the mentioned advantages. However, there are still some obstacles to its wide application.

- High cost
  At the current stage, the cost of bioplastic is two or three times higher than ordinary plastics [34], which hinders its rapid application. As it has not been widely used, bioplastic cannot be prepared in large quantities. If bioplastic obtain the mass production stage, the cost can be greatly reduced.

- Short of technology
  Bioplastic can be biodegraded has given a path which no longer relies on oil to produce plastic.
However, the technology of bioplastic production is still under development. In addition, some methods may generate carbon dioxide, which causes global warming.

- Limited supply of bioplastic
  
  To some extent, the price of biomass used to produce bioplastic is still governed by oil price. In order to maintain the stability of market, bioplastic production is still low. Moreover, exploiting oil may aggravate the decrease of non-renewable resources and cause more pollution.

- Low consumer awareness of biodegradable plastics
  
  Most customers do not know how to distinguish these materials such as biomaterials and biodegradable materials, or renewable materials and how to weigh the different attributes. Therefore, it is very important to strengthen the promotion to customers such as accurately interpreting the definitions of related terms.

- Lack of unified bioplastic labeling method
  
  Customers know little about how to deal with the waste of bioplastic. The bioplastic industry needs to make some rules about unified bioplastic labeling method for easily classifying, hence people can deal with the waste of bioplastic based on the categories.

- The end of life management for bioplastic
  
  Currently, there's no specific management method for the collection and treatment of bioplastic waste, which also limits the development of bioplastics. Furthermore, it may cause some new type of pollution if the exhausted bioplastic is not well managed.

- Toxicity
  
  When wastewater sludge was used as the raw materials for the production of bioplastic, there could be toxic compounds like some heavy metals and non-metal oxides in the sludge going to the bioplastic during the extraction. With the utilization of the products produced from bioplastic, the toxic materials could be released and cause a health threat.

5.3. The prospect of bioplastic

According Helmut Kaiser Consultancy’s report, the global bioplastic market will grow rapidly with an average annual growth rate of 8%-10%. It is expected to increase from 1 billion US $ in 2007 to 10 billion US $ by 2020 [35]. New applications in the automotive and electronics industries will drive growth in demand for bioplastic. Based on the rapid development of transgenic plants, Asia will be the market leader in the bioplastic market.

In the future, the increase in the share of bioplastic will mainly benefit from the improvement in the performance of technologies. Technological innovation will expand its application in the automotive, medical and electronics industries. According to its adapt to the body, bioplastic is expected to be used in the production of medical products such as postoperative sutures which can be absorbed by the body. Thus, the patients do not need to undergo the pain and risk of the second operation. Moreover, high consumer acceptance, danger posed by climate change, increasing price of fossil materials, and dependence on fossil resources are the driving forces of the bioplastic market. The wide variety of bioplastic applications under development is a positive factor for the growth of bioplastic which also helps to capture market share and huge consumption potentiality from competing materials. Due to the developments of new technologies, bioplastics are moving towards the mass market and having a brighter future [36].

6. Summary

Plastic products bring a series of environmental problems while satisfying human needs. To solve the problems of environmental pollution and resource scarcity, bioplastic has been proposed and developed. As a new type of material, bioplastic has been recognized by various countries for its environmental friendliness and reproducibility. Its advantages include low carbon emissions, biodegradability, energy conservation, and non-toxicity. Bioplastic can be divided into all-bioplastic and part-bioplastic according to the amount of biomass in bioplastic; natural bioplastic and synthetic bioplastic according to the production method of bioplastic; biodegradable bioplastic and non-
biodegradable bioplastic according to its biodegradability.

In the biological treatment of sewage, activated sludge can quickly convert the easily degradable substrate into PHA. Using this feature, the research on the synthesis of PHA from activated sludge has achieved certain results. Based on the complexity of the treatment process and bio-community structure of activated sludge, there are two important mechanisms to produce PHA, which are the Enhanced Biological Phosphorus Removal (EBPR) system and the aerobic dynamic feeding mode (Feast-Famine mechanism). However, these two methods did not meet the requirements sometimes. The researchers found that it was possible to combine the two methods to obtain better efficiency. Therefore, the third process for PHA synthesis was proposed, which could obtain more PHA production than that with Feast-Famine mechanism.

At present, bioplastic is used in many fields, such as the packaging industry, textile industry, manufacturing industry and the medical industry. However, its development also faces many challenges such as price issues, the technique needed to be improved, and the collection and treatment of its waste. Methods of synthesis and characterization can be used to solve the above problems [37-39].

In spite of above all, bioplastic is in great needs and we should study new methods to obtain it.

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