

Production of Biodegradable Plastics from the Palm Oil Mill Effluent (POME) by Photosynthetic Bacteria and Hydrogen Bacteria

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INTRODUCTION

Palm oil is mainly produced in the South East Asian region including Malaysia and Indonesia. More than 15 million tons of crude palm oil, more than 80% of the world supply, are exported from this area to the world. From palm oil industry in Malaysia more than 15 million tons of palm oil mill effluent (POME) is annually wasted. POME has a high carbon content (BOD higher than 20,000 ppm) and currently treated anaerobically in lagoons to produce bio-gas including methane which is uselessly released into the atmosphere(1, 2). Apart from the issue of the greenhouse effect by the gas, this method wastes carbonaceous matter that could be utilized for a profitable product. We have developed methods to utilize POME to produce bacterial biodegradable plastics, poly-hydroxyalkanoate (PHA) by photosynthetic bacteria and hydrogen bacteria (3-6). Recently, a total treatment system for the solid as well as liquid wastes from palm oil industry is proposed by Shirai and Hassan. Figure 1

summarizes this concept: This is based on a model palm oil mill which is representative mean sized one in Malaysian palm oil industry with 300 mills. Twenty seven thousand tons of crude palm oil is annually produced from 81,000 tons of palm oil bunch wasting 40,000 tons of POME and 29,000 tons of solid wastes. We focused on the POME treatment and PHA production from it. First POME is anaerobically treated to yield organic acids including acetic acid that can be used for the PHA production. To reduce the residence time of POME in the tank, activated sludge is separated and recycled to the anaerobic treatment tank. However, separating the sludge from the POME anaerobically treated is difficult because the particle size of sludge is too small to sediment easily by for example centrifugation. The POME anaerobically treated including around 10 g/l of organic acids is concentrated by evaporation to reduce the volume of the POME anaerobically treated and to obtain the

purged water.

The energy to concentrate the POME anaerobically treated is provided by burning the solid waste from palm oil industry. In the model mill 5,000 tons of the solid wastes are required to remove 39,000 tons of water from the POME anaerobically treated. The concentrated POME anaerobically treated is fed to a fermentor in which hydrogen bacteria are cultivated to accumulate PHA in the bacterial cell body from organic acids. The carbonaceous matter in the POME is finally converted to PHA with 50% of content in the cell. In our system the purged water is yielded mainly by evaporation and something valued is given to the sludge because PHA is contained in the sludge.

PURPOSE

In this system separation of sludge from POME anaerobically treated is an important issue to complete this system. Then efficient concentration of the POME anaerobically treated is also important because the concentration process is essential in this POME treatment system. We have previously examined to separate sludge by adding alkaline to the POME. However, the sludge separated should be with high pH and it is damaged by the high pH. By this method it is difficult to obtain effective sludge to improve the productivity of organic acids from POME. A freezing and thawing is one of the efficient separation method for sludge in a sewage treatment process. This year a freezing-thawing was applied to separate sludge including active bacteria from the POME anaerobically treated. A quite good results were obtained and the separated sludge could be used for the sludge recycled to the tank for anaerobic treatment, resulting in reducing POME residence time and enhancing the productivity of the POME anaerobically treated.

MATERIALS AND METHODS

Materials

Calcium carbonate and sodium hydroxide was used for adjusting a process pH during an anaerobic treatment of the POME. Another experiment utilized only sodium hydroxide for the pH adjustment. Analytical grade chemicals were used for the experiments.

Experimental Procedures

Production of POME anaerobically treated

First POME was treated anaerobically mixed with the sludge obtained from the bottom of a lagoon in a palm oil mill by a batch operation using a 10 liter plastic tank. After one week operation, POME was introduced to the anaerobic treatment tank to start a continuous operation with a POME residence time of 5 days. The pH was adjusted by a 1N sodium hydroxide solution. In another experiment around 0.1 % calcium carbonate was also added to adjust the pH.

Separation of Sludge from POME Anaerobically Treated by a Freezing and Thawing Method

The POME anaerobically treated that was withdrawn from the anaerobic treatment tank was frozen in a freezer at $-30\text{ }^{\circ}\text{C}$. The POME anaerobically treated was completely frozen. Then, ice bricks was put on a 60-mesh metal screen and thawed at a room temperature (around $25\text{ }^{\circ}\text{C}$). Both the POMEs obtained from a system with a pH adjustment by only sodium hydroxide and that with calcium carbonate as well as sodium hydroxide. The sludge separated was remained on the mesh screen and the POME with much less sludge was dripped down from the screen by thawing.

Recycle of the Sludge Separated from POME Anaerobically Treated

The sludge separated by a freezing and thawing method was recycled to the anaerobic treatment tank to reduce the POME residence time. The residence time was reduced at 2.5 days to continue the continuous operation. Once a day overflowed POME anaerobically treated was frozen in a freezer. Every day the separated sludge was mixed with POME that should be treated and introduced to the tank.

Analysis

Organic acids were identified by HPLC using aH^+ form cation exchange resin column (TSK GEL SCX (H⁺) 300 x 7.8 mm, Tosoh, Tokyo) and 7mM sulfuric acid as the mobile phase.

RESULTS AND DISCUSSION

Effect of Calcium Carbonate on the Separation of Sludge by Freezing-Thawing Method.

When an anaerobic treatment of POME was performed with a pH adjustment by only sodium hydroxide, no sludge was remained on the mesh screen and no sludge separation from POME anaerobically treated was achieved. When, however, another anaerobic treatment of POME was carried out with a pH adjustment by both sodium

hydroxide and calcium carbonate, more than 90% of the sludge was remained on the mesh screen as a form of spoonful ice cream. The sludge was easily separated from the POME anaerobically treated

Generally speaking, negative charges are distributed on the surface of the bacterial cells. The sludge mainly composes several bacteria which were survived in the POME under an anaerobic condition. Calcium cation has divalent positive charges and can cap the negative charges on the cells, yielding no electric charges and hydrophobicity on the cell surface. This enables cells to attach one another, resulting in forming a large cell agglomerate which easily sediments and sticks with other cell aggregates.

Moreover, freeze concentration occurs during freezing among ice crystals because ice crystals reject any other component except water molecules, resulting in concentrating other components outside ice crystals. Further ice crystallization proceeds the space outside ice crystals reduces and the sludge particles are compressed. When the anaerobic treatment of POME is carried out by a pH adjustment with only a sodium hydroxide solution bacterial cell surface would have still negative charges which make the cell particles difficult agglomerated. On the other hand, when the process pH was controlled by using both calcium hydroxide and sodium hydroxide, calcium cations contribute to reduce negative charges on the bacterial cell surface and hydrophobic cell surface promotes cell attachment. This is because a sludge aggregate remained on the mesh screen after the frozen POME anaerobically treated was thawed.

Anaerobic Treatment of POME with Recycling the POME Sludge

All the POME sludge on the mesh screen obtained by a freezing-thawing method was recycled to the anaerobic treatment tank. More than 90% of the sludge was recovered and reused for the POME treatment. The POME residence time was set at 2.5 days.

Figure 2 shows an experimental results, indicating that a constant production of organic acids including acetic, propionic and butyric acids under a steady condition. Around 10g/l of organic acids was produced at a steady state. We have previously attempted to operate an anaerobic treatment of POME with a POME residence time at 2.5 days without any recycling of the sludge. However, it was failed due to no steady state was obtained at all, as shown in Fig. 2. This difference is ascribed to the sludge recycling because bacterial concentration in the tank with sludge recycle is much more than that with no sludge recycle. It was confirmed that freezing-thawing is effective to separate the sludge from the POME anaerobically treated with a bio-activity which promotes anaerobic degradation of organic materials in POME to

organic acids including acetic acid.

Discussion

This research clearly indicates that calcium carbonate is essential to form sludge aggregate from the POME anaerobically treated by a freezing-thawing. It was confirmed that the freezing-thawing is effective to obtain biologically active sludge which can be recycled and enhance the organic acids productivity. In this process 90% of the sludge was recycled and 10% was wasted with calcium carbonate. The sludge with calcium carbonate can prevent pH from shifting an acid side and organic compounds in the sludge contribute to fertilize soils when they are put on farms. This would be able to contribute to enrich and neutralize acidic Malaysian soils.

Using calcium carbonate, moreover, could reduce the amount of sodium hydroxide to maintain the pH. Though sodium hydroxide is a cheap chemical, it is difficult to recover it from a reaction system. Therefore, reducing the amount of sodium hydroxide consumed is required to save the cost. Adding calcium carbonate reduced the amount of sodium hydroxide consumed. Calcium carbonate is also another cheap material and used for a fertilizer. Thus addition of calcium carbonate would give values to the POME treatment.

A freezing-thawing method requires electricity to freeze the POME anaerobically treated. The electricity can be obtained by using the solid wastes from palm bunches, trunks etc. for the electric power generation. The ice cold heat which is obtained from ice crystals thawed can be used for air conditioning in a palm oil mill to improve working amenity. So far, air conditioning in a palm oil mill might be an unnecessary and luxury facility, but it would be essential when Malaysia gets into a member of developed countries in the near future (2020).

CONCLUSIONS

1. Sludge was easily separated from POME anaerobically treated by a freezing and thawing method.
2. Calcium carbonate was necessary to promote sludge separation by forming aggregate from the sludge.
3. The separated sludge was recycled to an anaerobic treatment tank of POME to reduce the POME residence time and to enhance the organic acids productivity.
4. The sludge separated by a freezing and thawing maintained biological activity for the anaerobic treatment of POME.
5. The freezing-thawing method proposed in this research enables to treat POME as well as to produce organic acids which can be used for the biodegradable plastics

production as raw materials.

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