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Effect of polyhydroxyalkanoates on dark fermentative hydrogen production from waste activated sludge

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ARTICLE INFO

Article history:
Received 12 August 2014
Received in revised form
5 January 2015
Accepted 10 January 2015
Available online 20 January 2015

Keywords:
Hydrogen production from waste activated sludge
Dark fermentation
Biological nutrient removal
Polyhydroxyalkanoates

ABSTRACT

Polyhydroxyalkanoates (PHA), an intracellular energy and carbon storage polymer, can be accumulated in activated sludge in substantial quantities under wastewater dynamic treatment (i.e., substrate feast-famine) conditions. However, its influence on hydrogen production has never been investigated before. This study therefore evaluated the influences of PHA level and composition in waste activated sludge (WAS) on hydrogen production. The results showed that with the increase of sludge PHA content from 25 to 178 mg per gram volatile suspended solids (VSS) hydrogen production from WAS alkaline anaerobic fermentation increased from 26.5 to 58.7 mL/g VSS. The composition of PHA was also found to affect hydrogen production. When the dominant composition shifted from polyhydroxybutyrate (PHB) to polyhydroxyvalerate (PHV), the amount of generated hydrogen decreased from 51.2 to 41.1 mL/g VSS even under the same PHA level (around 130 mg/g VSS). The mechanism studies exhibited that the increased PHA content accelerated both the cell solubilization and the hydrolysis process of solubilized substrates. Compared with the PHB-dominant sludge, the increased PHV fraction not only slowed the hydrolysis process but also caused more propionic acid production, with less theoretical hydrogen generation in this fermentation type. It was also found that the increased PHA content enhanced the soluble protein conversion of non-PHA biomass. Further investigations with enzyme analyses showed that both the key hydrolytic enzyme activities and hydrogen-forming enzyme activities were in the sequence of the PHB-dominant sludge > the PHV-dominant sludge > the low PHA sludge, which was in accord with the observed order of hydrogen yield.

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http://dx.doi.org/10.1016/j.watres.2015.01.017

1. Introduction

The usage of fossil fuel is generally considered as unsustainable due to its diminishing supply and large contribution to greenhouse gas generation (Lingampalli et al., 2013). Meanwhile, waste activated sludge (WAS), which is a byproduct of biological wastewater treatment, is inevitably produced in huge quantities (Xu et al., 2012). Therefore, biological production of hydrogen from WAS has attracted much attention (Cai et al., 2004; Li et al., 2009; Zhao et al., 2010), by which fossil fuel is saved, WAS is reduced and reused, and the important renewable energy hydrogen is also achieved.

In general, the rate of hydrogen production from WAS is low, thus most of previous studies to date have focused on the enhancement of hydrogen generation efficiency via pretreating sludge (Yang et al., 2012; Assawamongkholsiri et al., 2013; Kim et al., 2013), controlling operational parameter (Saady, 2013; Gioannis et al., 2013; Zhou et al., 2013), and improving reactor design (Saady, 2013; Jung et al., 2011). For example, it was found that hydrogen production from WAS could be significantly enhanced by controlling fermentation pH at constant 10, because this strategy not only improved the hydrolysis process but also inhibited the activities of hydrogen consuming bacteria of both methanogens and acetobacteria (Zhao et al., 2010). Besides, it is known that WAS is a nitrogen-rich substrate with low carbon to nitrogen ratios (around 7/1) whereas the recommended C/N ratio for anaerobic fermentation system is 20/1 to 30/1 (Kim et al., 2012). Hence, several researches were performed to improve hydrogen yield through optimizing co-fermentation substrates. It was reported that the bioconversion of sludge protein and the yield of hydrogen could be largely increased by pertinent addition of carbohydrate-rich substrates, such as primary sludge, food wastes, and agricultural wastes to WAS fermentation reactors (Saady, 2013; Zhou et al., 2013; Kim et al., 2012; Chen et al., 2012; Liu et al., 2013). Despite these important progresses, the enhancement of hydrogen production from WAS by improving the self-characteristic of sludge has been seldom documented in the literature.

Polyhydroxyalkanoates (PHA), an intracellular metabolic intermediate and energy and carbon storage polymer in wastewater treatment processes, has the ability of rapid and complete degradation under anaerobic conditions (Reischwitz et al., 1998; Chen and Wang, 2002). PHA can be accumulated in the external substrate feast stage, but the accumulated PHA is easily consumed in the subsequent famine stage. As a result, its content in WAS wasted from the traditional wastewater treatment plants (WWTPs) is usually at low levels (Fig. S1, Supporting Information). When using this WAS for anaerobic fermentation, as mentioned above, the rate of hydrogen production is low. Recently, there have been increasing evidences showing that WAS with high levels of PHA can be obtained in WWTPs either by process improvement or by operation optimization. Takabatake et al. (2002) reported that activated sludge biomass from 4 real WWTPs had the capability to accumulate PHA up to 18.8% of dry cell weight on average, with the range of 6.0%–29.5%. Coats et al. (2007) found activated sludge consortiums capable of synthesizing PHA at 10–25% when fed with primary solid fermented liquors. Based on the results, they further proposed a side-stream process for both PHA production and wastewater treatment. In our recent studies, it was observed that PHA content in WAS withdrawn from a biological phosphorus removal reactor reached 116 ± 5 mg per gram volatile suspended solids (VSS) by wasting sludge at 1 h of aeration (Wang et al., 2013).

The increase of PHA content in WAS might cause the changes of sludge characteristics, which further affected the subsequent anaerobic fermentation. To date, however, the influence of PHA on hydrogen production from WAS has never been reported. Some scientists suggested that the microbial cells would become more fragile with the increase of intracellular PHA (Budwill et al., 1992; Page and Cornish, 1993; Lee, 1996). Thus, it is presumed that the increased PHA in WAS might be beneficial to hydrogen production. If this hypothesis is clearly supported by experimental evidences, a new door may be opened for both wastewater treatment and hydrogen production from WAS. That is, organic pollutants in wastewaters are designed to be primarily removed via PHA accumulation, and then the WAS with high levels of PHA is used for hydrogen production, by which aeration cost in wastewater treatment process is saved, WAS amount is reduced, and hydrogen yield in WAS anaerobic fermentation is enhanced.

The aim of this paper was to provide a deep understanding of PHA associated with hydrogen production in dark fermentation. First, the influences of PHA level and composition in WAS on anaerobic hydrogen production were investigated in batch tests at pH 10. It was reported that alkaline conditions (especially pH 10) were beneficial to hydrogen production from WAS (Cai et al., 2004; Zhao et al., 2010), because this method not only enhanced the hydrolysis process but also inhibited the activities of hydrogen consuming bacteria (Zhao et al., 2010). Then, the reasons for PHA affecting the yield of hydrogen production were explored from the aspects of the microbial cell disruption, solubilized substrate hydrolysis, acidification of hydrolyzed products, fermentation type, mass balance, and activities of key enzymes.

2. Materials and methods

2.1. *The source of sludges with different PHA contents*

The following activated sludge bioreactors were performed to culture the sludges with different PHA contents as such characteristic sludges are not available now in real WWTPs. Seed sludge was taken from the secondary sedimentation tank of a municipal WWTP in Shanghai, China, and was concurrently inoculated into five identical sequencing batch reactors with a working volume of 40 L each. All reactors were carried out the same and operated with four cycles (6 h per cycle) daily. Each cycle consisted of a 240 min aerobic period, a 55 min settling period, a 5 min decanting period, and a 60 min idle period. During the aerobic period, air was supplied into all reactors at a flowrate of 20 L/min. To obtain sludges with different PHA contents, these reactors received 200, 400, 600, 800, and 1000 mg/L of influent chemical oxygen demand (COD)