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Characteristics of biohydrogen fermentation from various substrates

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ABSTRACT

The characteristics of biohydrogen production from sucrose, slurry-type piggery waste and food waste under the effects of the reactor configurations and operational pHs (6 and 9) were examined by using heat-treated anaerobic sludge as a seed biomass. When sucrose was used in the batch test, the maximum hydrogen yield was 0.12–0.13 g COD (as H_2)/g COD (1.41–1.43 mol/mol hexose) at pH 6. In contrast, 0.10–0.11 g COD (as H_2)/g COD (1.12–1.21 mol/mol hexose) hydrogen yield was achieved from the reactor at pH 9. On the other hand, hydrogen production was not observed in the continuous sequencing batch mode fermenters fed with sucrose. Profile analysis at each cycle revealed hydrogen production at the initial operation periods but eventually only methane at 36 days. When slurry-type piggery waste was used as the substrate, the upflow elutriation-type fermenters produced methane but not hydrogen after 30 days operation. The fermentation intermediate profile showed that the hydrogen produced might have been consumed by homoacetogenic or propionate producing reactions, and eventually converted into methane by acetoclastic methanogens. The downflow leaching bed fermenters using food waste produced 0.013 L H_2/g volatile solids (VS) (0.0061 g COD (as H_2)/g COD) at pH 6 with 54% VS reduction whereas 0.0041 L H_2/g VS (0.0020 g COD (as H_2)/g COD) was produced at pH 9 with 86% VS reduction. The results show that the hydrogen produced should be released rapidly from the reactor before it can be consumed in other biochemical reactions, and substrates with high pH level (>9.0) can be used directly to produce hydrogen without needing to adjust the pH.

1. Introduction

The increasing cost of fossil fuels and pollutants are increasing concerns that have prompted extensive searches for alternative energy sources [1]. Greenhouse gases resulting from fossil fuels may cause climate change and future energy scarcity. As part of an ongoing search for alternative energy sources, research on renewable energy production including

Abbreviations: BA, bicarbonate alkalinity; COD, chemical oxygen demand; CSBF, continuous sequencing batch fermenter; CSTR, complete stirred tank reactor; DLBF, downflow leaching-bed fermenter; HAc, acetic acid; HBu, butyric acid; HFr, formic acid; HPr, propionic acid; HRT, hydraulic retention time; HVa, valeric acid; ICOD, insoluble chemical oxygen demand; Lac, lactic acid; OLR, organic loading rate; SCOD, soluble chemical oxygen demand; TCOD, total chemical oxygen demand; TS, total solids; UEF, upflow elutriation-type fermenter; UASB, upflow anaerobic sludge blanket; VFA, volatile fatty acids; VS, volatile solids.

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hydrogen is actively progressing. Hydrogen is an alternative energy, in which the combustion end-product is water. Hydrogen contains a high energy yield of 122 kJ/g and 2.7 times the energy intensity than fossil fuels and can also be used to generate electricity via fuel cells [2,3].

Biological hydrogen production can be more environmental friendly and less energy intensive than chemical process [4], and has been studied using reactor configurations, such as CSTR, and UASB [5,6]. In CSTR it is more favorable to wash out methane-producing bacteria by selecting short retention time, while UASB is more tolerate to the fluctuation of environmental parameters including organic loading rates. However, the performance of a CSTR revealed unstable hydrogen production due possibly to variations in the organics and fatty acids in the reactor [7]. The important operational parameters to maximize the hydrogen production in anaerobic fermentation include pH, temperature, substrate concentration, HRT and incubation conditions. Stable hydrogen production is achieved under the optimal operation conditions, whereas the level of hydrogen produced from fermentation has been reported to vary under the same operating conditions [4,8–10].

pH is one of critical parameters affecting biological hydrogen production because pH affects the metabolic pathway of hydrogen-producing organisms [11,12]. Most studies on the maximum hydrogen yield proposed a low pH between 5 and 6 [13–16] because the methanogenic activity is limited to a narrow pH between 6.5 and 7 [17,18]. On the other hand, some actual substrates (as alternative energy sources) often have high pH levels (for example, >pH 8.5 for piggery waste). In terms of practical applications, it is important to determine on how the initial influent pH affects hydrogen production when there is no pH control during hydrogen fermentation.

Biohydrogen fermentation studies have been limited to dissolved organics as substrate. Carbohydrates, such as glucose, sucrose and liquid waste, have been used to produce hydrogen, and comparisons of the yield and conversion rate have been conducted generally in batch tests [13,19]. On the other hand, particulates and solids, which mostly exist in the surrounding environment, can be an attractive hydrogen source. With piggery waste (as particulates), there is some difficulty in separating the supernatant and a high level of refractory organics, such as crude fiber and lignin [20]. The use of piggery waste as an alternative energy source has the simultaneous advantages of energy production and waste treatment. The production of food waste (as solids) is approximately 0.3 kg/capita/d/(14,000 tons/d), and includes 29% domestic waste in South Korea [21]. The high cellulose contents and salinity in food waste creates difficulties for fertilizer products and composting. Food waste, however, can be a potential bioenergy substrate as well because it contains organic matter, which is a major source of hydrogen production [22]. For these higher solid wastes, hydrolysis and acidogenesis are an important step to produce the maximum biohydrogen by organic acids. Therefore, there is still a barrier to apply batch parameters in a full scale hydrogen production facility.

This study examined the effects of the initial pH (6 or 9) for practical hydrogen production using a range of substrates, such as soluble-type synthetic carbohydrate wastewater (sucrose) and slurry- (piggery waste) and solids-type actual wastes (food waste). In this experiment, different types of reactor configuration, including continuous sequencing batch mode, upflow elutriation-type or downflow leaching bed-type, were designed according to the characteristics of substrate based on previous studies [20,23,24], and examined to improve gas–liquid–solids separation in the reactor and to maximize the hydrogen yield efficiency.

2. Materials and methods

2.1. *Inocula and substrates*

2.1.1. *Seed sludge*

Anaerobic sludge from a local brewery wastewater treatment plant (Gwangju, S. Korea) was used as the inocula in this study. The anaerobic sludge was heat shocked (baked) at 105 °C for 2 h to avoid hydrogen-consuming organisms before seeding [25]. The concentration of anaerobic sludge was 26 g VSS/L with 0.88 VSS/TSS ratio. The heat-treated anaerobic sludge was used for all reactors in this experiment and there was no heat treatment for substrates.

2.1.2. *Synthetic carbohydrate wastewater*

Soluble-type synthetic carbohydrate wastewater was prepared using sucrose for a batch activity test and continuous sequencing batch fermenter (CSBF). Sucrose, an easily biodegradable carbohydrate, was selected because the fermentation pathway is well-established. In the batch mode test using sucrose, a nutrient stock solution (20 ml per L influent) was added to the nutrient solution. The nutrient stock solution consisted of 13.61 g/L KH_2PO_4, 49.20 g/L NH_4Cl, 4.44 g/L $CaCl_4$, 8.13 g/L $MgCl_2 \cdot 6H_2O$ and 10 ml/L of a trace element solution with 19.44 g/L $FeCl_3$, 4.74 g/L $MnCl_2 \cdot 4H_2O$, 3.27 g/L $ZnCl_2$, 2.05 g/L $CuCl_2 \cdot 6H_2O$, 2.86 g/L $CoCl_2 \cdot 6H_2O$, 1.15 g/L $Na_2B_4O_7 \cdot 10H_2O$, 176 g/L $Na_3C_6H_5O_7$, 2.08 g/L $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 3.00 g/L $NiCl_2 \cdot 6H_2O$ [26]. The initial pH in the batch activity test was adjusted to 6 (known as the optimal hydrogen production) and 9 (for wastes with high pH level) using 1N-HCl and 1N-NaOH, and the control reactor did not contain substrate, acid and base. With the exception of pH, each reactor contained 30 ml of the inocula, 4 ml of sucrose (255 g/L) and 66 ml of a nutrient solution. For continuous-sequencing batch mode (CSBF) operation, 20 g/L sucrose was added to the influent with the nutrient solution (20 ml/L).

2.1.3. *Slurry-type piggery waste*

Raw slurry-type piggery waste collected from the inlet of a livestock wastes treatment plant (Sangju, S. Korea) was used for the upflow elutriated hydrogen fermentation (UEF). The characteristics of the piggery waste are as follows: 35 g COD/L, 0.44 ICOD/TCOD ratio, 24.4 g/L of TS, 0.63 VS/TS ratio, 8.7 pH and 9.0 g $CaCO_3$/L. The pH-amended (pH 6) and raw slurry-type piggery wastes (pH 8.7–9) were prepared based on this experiment.

2.1.4. *Food waste*

Food waste was collected from the inlet of a food waste treatment facility (Daegu, S. Korea) prior to mechanical