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Biohydrogen production from starch wastewater and application in fuel cell

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ABSTRACT

Biohydrogen was produced from starch in wastewater by anaerobic fermentation. The effects of parameters, such as pH, starch concentration were investigated and optimum operating conditions were determined. The optimal pH and starch concentration for hydrogen production at 37 °C were 6.5 and 5 g/L, respectively with a maximum hydrogen yield of 186 ml/g-starch. The produced biogas contains 99% of hydrogen after passing through KOH solution to remove CO_2. The anaerobic fermentation installation was integrated with a proton-exchange-membrane fuel cell (PEMFC) system for on-line electricity generation. This combination system of biohydrogen and fuel cell achieved a power output of 0.428 W at 0.65 V per cell.

1. Introduction

Hydrogen is considered to be an ideal clean energy source, producing water as its only by-product when it burns. Hydrogen is traditionally produced by hydrocarbon fermentation or electrolysis of water [1]. These processes require external energy sources for producing the hydrogen and therefore expensive. Biohydrogen production is more economical and environmentally friendly than that of traditional method with biomass converted to hydrogen [2–6].

Hydrogen production by anaerobic fermentation using organic waste as the substrate has drawn much attention since this system requires low energy input and low costs. H_2 and CO_2 are the main products and organic acid and alcohols are the by-products. Microbial hydrogen production through anaerobic fermentation not only yields the bioenergy but also treats the wastewater with product recovery [7–9]. It is a developing trend that hydrogen or other bioenergy is produced by an environmentally friendly manner.

According to previous studies, the efficiency of anaerobic digestion is related to both the operating conditions and process control. The rate of hydrogen evolution from an anaerobic fermentation depends on several parameters such as pH, substrate concentration and so on [10–12]. However, less information is available for the relationship between hydrogen production, pH value, and substrate concentration in an anaerobic fermentation process due to the lack of understanding of the mechanism of hydrogen production. Therefore, in this study, the effect of the pH on the anaerobic biohydrogen production procedure was investigated through the operation of three different reactors.

One of the most critical issues for commercial application of biohydrogen is storage and transportation. However, the storage of H_2 is a difficult problem at present and limits the commercialization of hydrogen technology. It is important to find a commercially viable procedure and cheap method for the application of H_2. One of the possible methods to resolve this difficulty is the combination of biohydrogen product with fuel cells, in which the hydrogen produced from anaerobic

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fermentation is transferred directly to proton-exchange-membrane fuel cell (PEMFC) for electricity production. This procedure of storage and transportation for hydrogen is omitted. Until now, there are few reports of combining the biohydrogen and fuel cell for electricity production [13,14].

In this study, the conditions of anaerobic fermentation were studied in order to understand the effects of the operating conditions and process control on hydrogen production. Effect factors such as pH and starch concentrations were investigated for determining the optimum operation conditions at hydrogen production. The combination system of anaerobic fermentation with fuel cell was investigated and developed.

2. Materials and methods

2.1. *Hydrogen-producing seed sludge*

The seed sludge was taken from the recycled stream after the bio-treatment stage of a municipal wastewater treatment plant in Guangdong, China. The pH value of the seed sludge was around 6.8. The chemical oxygen demand (COD) of the seed sludge was 4127 mg/L. The seed sludge was kept under anaerobic condition for several days before being used without any pretreatment.

2.2. *Experimental conditions*

Three series of batch experiments were conducted in 500 ml conical flasks at 37 °C. Volumes of 300 ml medium and 60 ml sewage sludge were added to the flasks. Then, the flasks were purged with nitrogen for 2 min to create an anaerobic condition. Magnetic-stirring was also employed in the experiments. The medium was prepared with starch as the sole carbon source, containing the following nutrients in g/L: peptone, 0.75; KCl, 1.5; $NaH_2PO_4 \cdot 2H_2O$, 0.03.

The biogas release from anaerobic fermentation reactor was sent into a CO_2 absorber for removing CO_2. Then, the purified H_2 was introduced into a home-made PEMFC for electricity generation.

2.3. *Analytical method*

The biogas volumes were measured at normal temperature (25 °C) and pressure (760 mmHg). The fraction of hydrogen, methane and carbon dioxide was determined with a gas chromatograph (Kexiao 1690T, Hangzhou, China) equipped with a thermal conductivity detector. A 1-m stainless column packed with TDX-01 was used in the gas chromatograph. Nitrogen flowed at the rate of 30 ml/min as the carrier gas. The operation temperatures of the injection port, the column, and the detector were maintained at 80, 60 and 100 °C, respectively. The pH was measured with a pH meter (PHS-2C Shanghai, China).

3. Results and discussion

3.1. *Effect of initial pH*

In order to understand pH effect on hydrogen production, a series of fermentation tests were conducted by anaerobic fermentation for the conversion of starch into hydrogen at different initial pHs. The results showed that the initial pH affected all the kinetic parameters.

As indicated in Fig. 1 (curve a) the H_2 producing activity occurred at a wide pH range of 5–7.5. The H_2 yield appeared to increase from 5 to 6.5 and then decreased as the pH further increased from 6.5 to 7.5. The maximum hydrogen yield of 186 ml/g-starch at pH 6.5 was higher than an earlier reported value of 120 ml/g [15]. When the pH was low 3.5, it is observed no hydrogen was produced since the activity of hydrogen production bacterial was inhibited at low pH. This result suggested that the activity of the hydrogen production bacterial was inhibited by the low pH degree, and there were much volatile fatty acids (VFAs) accumulated. One report [16] observed that hydrogen production occurred at a low pH value of 4.5, but Zhang et al. [17] studied that when the pH value less than 4, hydrogen production was stopped and only VFAs production proceeded.

Therefore, pH is a fundamental operating parameter for the production of hydrogen [17–21]. In this study, the trend of pH dependence is in close agreement with some previous results [19,20,24], in which a pH of 5.5–6 was the optimum initial pH for hydrogen production. The results were different from reference [15] in which the highest yield occurred at pH 7.5–8.0. According to literature, the range of optional pH varied from 4.5 to 7.5 [17–23,25]. This fact can be explained that the different pH dependence of hydrogen production may primarily be attributed to the difference in the dominant bacterial H_2 producing population present in a mixed culture.

Fig. 1 (curve b) shows the relation of initial pH and final pH in anaerobic fermentation using starch in wastewater as fermentation carbon source. The final pH values from 3.3 to 3.6 correspond to initial pHs of 5–7.5.

Some volatile fatty acids (VFAs) produced during the production of hydrogen leads to a decrease of pH value. Therefore, the hydrogen production was inhibited at low pH value. This explanation can also be supported by an experiment using a phosphate-buffered medium as the fermentation solution and the pH value was maintained with hydrogen production time extended.

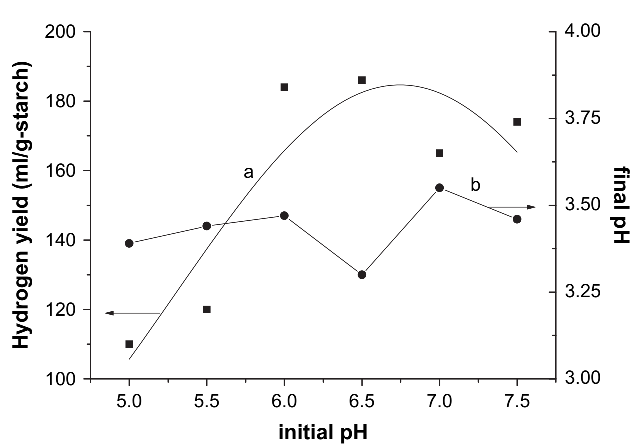

Fig. 1 – Hydrogen yield (curve a) (ml/g-starch) and final pH (curve b) versus initial pH at starch concentration 5 g/L with maximum hydrogen yield at pH 6.5.

3.2. *Effect of starch concentration on hydrogen production*

Fig. 2 shows the influence of starch concentration varying from 1 g/L to 7 g/L in wastewater.

It is observed that hydrogen yield increased with starch concentration in wastewater from 1 g/L to 5 g/L. However the hydrogen yield decreased when starch concentration increased from 5 g/L to 7 g/L. The decrease in hydrogen yield at higher starch concentration attributes to the increase in total Vass leading to rapid decrease of pH, which can inhibit further production of hydrogen. This result is consisting with a previous study [15].

3.3. *H_2 production rate*

The biogas production rate was investigated at the discontinuous experimental condition. As can be seen from Fig. 3, the rate of hydrogen production was high at the initial stage of anaerobic fermentation at the optimum pH 6.5, and reached its maximum at 22.5 ml/L. After 1 h, the rate of hydrogen production reduced gradually since the VFAs production leading to the decrease of pH value. This experiment results suggest that it is required to maintain pH stable during the anaerobic fermentation procedure.

3.4. *COD removal*

In a traditional anaerobic wastewater treatment process, chemical oxygen demand (COD) was mainly reduced through the conversion of intermediate products (e.g. acetic acid) to methane by the methanogenic microbes [26]. During hydrogen production process, COD was lowered through gas releases. Usually, COD removal is below 20% during hydrogen production process, which corresponds to a mean hydrogen production of 2.5 mol/mol glucose [27]. In this study with a raw solution COD of 4864 mg/L, the COD removal efficiency reached 64%, higher than earlier reported [26] value of 24.3 ± 9.1% of. Much higher COD removal of 82% was obtained in a previous study [28], in which pH 7.0 was maintained with a phase-separated two-stage anaerobic process employed and both hydrogen and methane were produced.

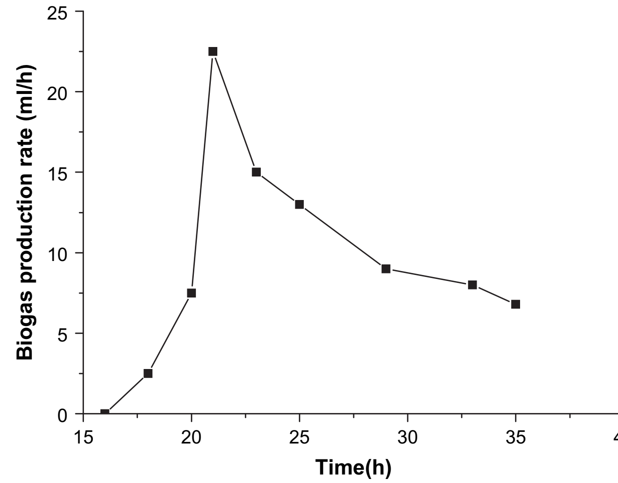

Fig. 3 – Biogas production rate versus biogas production time.

3.5. *PEMFC-integrated biohydrogen generation system*

The difficulty of storing and transporting biohydrogen limits its commercial application. This problem can be solved by combining the biohydrogen-producing system with fuel cell system for electricity generation. In this study, the biohydrogen produced by anaerobic fermentation was transported directly to a home-made proton-exchange-membrane fuel cell (PEMFC) for on-line electricity generation. The deposit and transportation of biohydrogen were omitted. However, there is little information in the literature referred to direct fuel cell electricity generation from biohydrogen [13,14].

Fig. 4 shows the time-output power profile generated by the home-made small PEMFC (2-cell stack, 10 cm^2) through

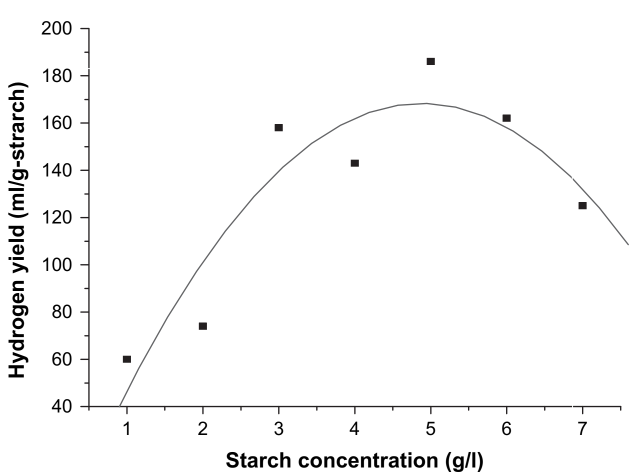

Fig. 2 – The correlation between hydrogen yield (ml/g-starch) and starch concentration at initial pH 6.5 with maximum hydrogen yield at starch concentration 5 g/L.

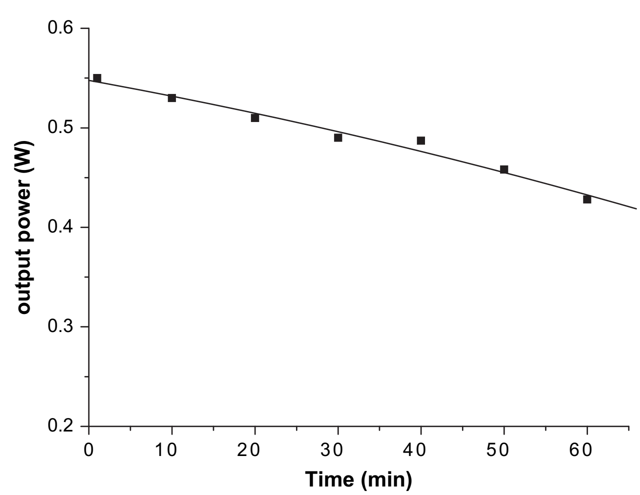

Fig. 4 – The time-output power profile generated by an in-house small PEMFC (2-cell stack, 10 cm^2) through a 2 kΩ external loading fed with biogas.

a 2 kΩ external loading using biogas as fuel. This fuel cell achieved a power output of 0.428 W at 0.65 V per cell after 1 h. The experimental result indicated that the purity and moisture of the biogas released from anaerobic fermentation was a suitable fuel for the fuel cell application. The advantage of this study is that the relationship of energy recovery of wastewater and electricity generation. Biohydrogen associating with fuel cell carried out on-line electricity generation will be more feasible for its commercial application.

4. Conclusions

This work demonstrates that the combination of anaerobic biological hydrogen production system and fuel cell system is feasible. The biohydrogen produced from starch in wastewater by anaerobic fermentation was transported directly to PEMFC for electricity generation. It was found that initial pH has an effect on hydrogen production. The optimum pH of wastewater was 5.5–6.0. The starch concentration was another important control parameter; the maximum hydrogen production was obtained when the starch concentration was controlled at range of 3–6 g/L.

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