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Continuous hydrogen production from cassava starch processing wastewater by two-stage thermophilic dark fermentation and microbial electrolysis

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ABSTRACT

Hydrogen production from cassava starch processing wastewater by two-stage thermophilic dark fermentation and microbial electrolysis was investigated. Single-chamber membrane-free microbial electrolysis cell with applied voltage of 0.6 V was optimum for hydrogen production with hydrogen yield of 245 ml H_2 $gCOD^{-1}$. Continuous microbial electrolysis reactor has a maximum hydrogen yield of 182 ml H_2 $gCOD^{-1}$ at HRT of 48 h with energy recovery efficiency of 217%. The continuous integrated two-stage dark fermentation and microbial electrolysis have hydrogen yield of 465 ml H_2 $gCOD^{-1}$ with 2 times hydrogen yield improving compared with a single stage and a maximum COD removal of 58% was achieved. Dominated bacteria at an anode of microbial electrolysis cell were exoelectrogens belong to *Brevibacillus* sp. *Caloranaerobacter* sp. and *Geobacillus* sp. Continuous two-stage thermophilic dark hydrogen fermentation and microbial electrolysis were efficient processes for hydrogen production from cassava starch processing wastewater.

Introduction

Hydrogen is an attractive energy carrier due to its potential for higher efficiency of conversion to usable power, low generation of pollutants and high energy density [1]. It is possible to produce hydrogen from organic waste, wastewater through fermentation using microorganisms, which has proven to be a relatively simple and inexpensive process [2]. Dark hydrogen fermentation process has high hydrogen production rate. Moreover, various organic waste materials such as food waste, rice straw, cheese whey, corn stalk waste and cassava starch processing wastewater can utilize for hydrogen gas production by dark fermentation process [3]. The hydrogen yield

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from dark fermentation of organic waste such as vegetable kitchen waste, palm oil mill effluent, co-digestion of food waste and sewage sludge, cassava pulp hydrolysate and starch were 38 [4], 340 [5], 123 [6], 342 [7] and 125 [8] ml H_2 $gCOD^{-1}$, respectively. Thermophilic dark fermentation is energetically more favorable for biological H_2 production and higher H_2 yield than mesophilic dark fermentation [9]. The promising advantage of thermophilic dark fermentation is better hydrogen production rate and enhances the hydrolysis rate of the complex substrate. In addition, thermophilic can more effectively utilize complex carbohydrates such as cellulose and starch [10].

Successful hydrogen production from cassava starch processing wastewater by dark fermentation was achieved under thermophilic conditions. Xie et al. [11] obtained the continuous hydrogen production rate and yield were 3.45 L H_2 $l^{-1}d^{-1}$ and 130 ml H_2 $gCOD^{-1}$ by mixed culture under thermophilic conditions (55 °C) at optimum values of 2 days HRT and OLR of 25.2 g COD l^{-1} d^{-1} in the anaerobic sequencing batch reactor (ASBR). In conventional hydrogen fermentation process could recover only 30–35% of the energy containing an organic waste converting to hydrogen. The rest of the energy remains in the liquid as VFA mainly butyric acid, acetic acid, lactic acid and propionic acid about 65–70% of the energy containing the organic waste. Microbial electrolysis process can convert acetic and butyric acid to hydrogen gas in a device called a microbial electrolysis cell (MEC). In an MEC, bacteria attached to an anode oxidize acetic and butyric acid, releasing electrons via a circuit to the cathode where hydrogen can be formed from protons in water [12]. Two-stage processes which integrated thermophilic dark fermentation with microbial electrolysis cell which eventually helps in improving gaseous energy recovery [13]. In addition, dark fermentation well complements MEC because fermentation efficiently breaks down complex forms of organic compounds into simple acids that anode-respiring bacteria can utilize in MEC [14]. Lu et al. [15] reported that an overall hydrogen recovery of 96% of the maximum theoretical yield of 0.125 g H_2 g COD^{-1}. Wang et al. [16] also reported that 41% increase in overall hydrogen yield from cellulose by integrated fermentation with MEC. However, integrated thermophilic dark fermentation with thermophilic microbial electrolysis cell is still a lack of information, especially for continuous operation.

In this study, the potential of hydrogen production from cassava starch processing wastewater was demonstrated using a two-stage thermophilic dark fermentation and thermophilic microbial electrolysis cell. The continuous operation of two-stage thermophilic dark fermentation and thermophilic microbial electrolysis from cassava starch wastewater processing using two phase up-flow anaerobic sludge blanket reactor was investigated.

Materials and methods

Feedstocks and inoculums

The cassava starch processing wastewater (CSWW) used in this study collecting from National Starch and Chemical Co., Ltd., Kalasin, Thailand. CSWW was stored at the temperature of 4 °C for later use. The physiochemical characters of the cassava starch processing wastewater and hydrogen production effluent were shown in Table 1. *Thermoanaerobacterium thermosaccharolyticum* PSU-2 was used for hydrogen production by thermophilic dark fermentation [13]. The stock culture of *T. thermosaccharolyticum* PSU-2 was maintained in synthetic medium containing starch soluble 2.0 g, yeast extract 1.0 g; NH_4NO_3 1.0 g; KH_2PO_4 1.0 g; K_2HPO_4 1.0 g; $MgSO_4{\cdot}7H_2O$ 0.2 g; $FeCl{\cdot}6H_2O$ 0.05 g; $CaCl_2$ 0.02 g and resazurin 0.5 mg in 1 L of deionized water. The pH of the medium was adjusted to 6.5 by adding 3 M HCl or 3 M $NaHCO_3$ and incubated at 55 °C [17]. The medium was flushed with nitrogen gas for 3–5 min to obtain completely anaerobic conditions. The bacteria inoculum in the MEC was thermophilic mixed culture enriching from peatland soil. The MEC was inoculated with a 1:1 (v/v) thermophilic mixed culture from peatland soil and basal anaerobic medium contained sodium acetate 2.0 g, yeast extract 1.0 g; NH_4NO_3 1.0 g; KH_2PO_4 1.0 g; K_2HPO_4 1.0 g; $MgSO_4{\cdot}7H_2O$ 0.2 g; $FeCl{\cdot}6H_2O$ 0.05 g; $CaCl_2$ 0.02 g and resazurin 0.5 mg in 1 L of deionized water [17].

Microbial electrolysis cell

Single-chamber membrane-less MEC was constructed to investigate the hydrogen production from thermophilic dark fermentation effluent. The system was made from glass bottles (120 ml) with working volumes of 40 ml. The bottles were closed tightly by silicone to avoid any gas leakage. The electrodes were immersed inside the bottles containing thermophilic dark fermentation effluent. The MEC systems were connected with the DC power supplier by platinum wires. The thermophilic dark fermentation effluent was obtained from cassava starch processing wastewater containing at 10 g COD L^{-1} operation. The effect of voltages on MEC performance for hydrogen production was investigated by applied voltages from 0.1 V to 0.8 V.

A continuous up-flow membrane-less MEC consisted of a graphite fiber felt anode (20 mm diameter, 150 mm length, 144 cm^2 surface area) and copper wire cathode. The total reactor volume was 435 ml (a 400 ml chamber; 5.5 cm diameter × 17 cm length and 35 ml headspace for gas collection). The reactor was closed tightly by silicone rubber stoppers and sealed carefully using silicone to avoid any gas leakage. The temperature of 55 °C was maintained by circulating water from a water bath heating. The anode biofilms of

Table 1 – Chemical characteristic of cassava starch processing wastewater (CSWW) and dark hydrogen fermentation effluent.

Parameters	CSWW	Dark fermentation effluent
Chemical oxygen demand (COD) (g L^{-1})	21.60	6.70
Total carbohydrate (g L^{-1})	16.12	2.51
Total solid (TS) (%)	16.66	11.70
Volatile solid (VS) (%)	9.37	7.43
pH	5.33	5.80
Volatile fatty acid (VFA) (g L^{-1})	0	1.23

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