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Hydrogen and Methane Production from Biodiesel Wastewater with Added Glycerine by Using Two-Stage Anaerobic Sequencing Batch Reactor (ASBR)

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In this work, a simultaneous production of hydrogen and methane from biodiesel wastewater with added glycerine was investigated by using a two-stage anaerobic sequencing batch reactor (ASBR) system. The hydrogen and methane reactors with 4 and 24 L of working volumes, respectively were operated under mesophilic temperature (37 °C) and 6 cycles per day while the pH in the hydrogen reactor was controlled at 5.5. The glycerine was added to the biodiesel wastewater at 3.5 %w/v to obtain a constant feed COD of 45,000 mg/L. A recycle ratio of 1:1 was used to minimize an NaOH addition in the hydrogen reactor for pH adjustment. The two-stage ASBR system was operated at different COD loading rates (ranging from 33.75 to 84.38 kg/m^{3}d based on the hydrogen ASBR system or 5.63 to 14.06 kg/m^{3}d based on methane ASBR system) in order to study the effect of organic loading rate on both hydrogen and methane production. The highest hydrogen and methane production performance was found at a COD loading rate of 67.50 kg/m^3 d and 11.25 kg/m^3 d based on hydrogen and methane reactors, respectively.

1. Introduction

Glycerol or glycerine is a main byproduct obtained from biodiesel production processes. Because of its over supply, the price of glycerine trends to go down. To increase the price of glycerine, several purification methods including filtration, chemical addition, and fraction vacuum distillation are employed but they have high energy consumption, leading to uneconomical operation (Thompson and He, 2006). Hence, attempts have focused to convert anaerobically glycerine to hydrogen (Chonga et al., 2009) and to methane (Fountoulakis and Manios, 2009). In this work, the simultaneous production of hydrogen and methane from biodiesel wastewater with added glycerine was investigated using a two-stage anaerobic sequencing batch reactor (ASBR) system. To maximize both productions of hydrogen and methane, the first ASBR was controlled at a constant pH of 5.5 with a recycle ratio of 1:1. The system was operated at different COD loading rates in order to determine an optimum COD loading rate for maximum production of both hydrogen and methane.

2. Experimental

2.1 Seed sludge preparation

Two samples of the seed sludges taken from the activated sludge unit of a biodiesel plant of Bangchak Biofuel at Ayudtaya and the anaerobic pond of a palm oil plant of Suksomboon palm oil at Chonburi were mixed and then screened to remove large solid particles. The mixed sludge was used to start up both bioreactors by adding to have an initial microbial concentration in terms of mixed liquid volatile suspended solids (MLVSS) about 12,000 mg/L.

2.2 Biodiesel wastewater

The biodiesel wastewater and glycerine were obtained from Bangchak Biofuel, Ayudtaya. A fixed amount of glycerine (3.5 %w/v) was added into the biodiesel wastewater to obtain a chemical oxygen demand (COD) of 45,000 mg/L. However, the amounts of nitrogen and phosphorous were not sufficient for *Table 1:*

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Chemical characteristics of the biodiesel wastewater with added 3.5%w/v glycerine

Parameter	Concentration	
Chemical oxygen demand (COD)	45,000	mg/L
Total suspended solids (TSS)	11,000	mg/L
Total nitrogen	1,200	mg/L
Total phosphorus	300	mg/L
Glycerine	27,700	mg/L

anaerobic fermentation (theoretical ratio of COD:N :P is 100:1:0.4) and so ammonium hydrogen carbonate (NH_4HCO_3) and di-potassium hydrogen orthophosphate (K_2HPO_4) were added. Table 1 shows the chemical characteristics of the studied wastewater.

2.3 ASBR operation

Figure 1 shows the two-stage ASBR system used in this study with liquid working volumes of 4 and 24L for the hydrogen and methane ASBR units, respectively. The two-stage ASBR system was operated at 37°C and 6 cycles per day. Each operational cycle consisted of 15 min feed, 90 min react, 120 min settle, and 15 min decant. The pH of the hydrogen ASBR unit was maintained constant at 5.5 by using a pH controller while the methane ASBR unit was operated without pH control. To minimize the amount of added NaOH used for the pH control of the hydrogen ASBR unit, a recycle ratio (the flow rate of final effluent from the methane ASBR unit to feed flow rate) of 1:1 was used to operate the studied ASBR system at different COD loading rates. For each COD loading rate, the studied system was operated to reach steady state before taking the samples of effluents and produced gas streams for measurement and analysis.

2.4 Measurements and analytical methods

A wet gas meter (Ritter, TGO5/5) was used to measure the volume of produced gas at room temperature. The gas composition was analyzed by a gas chromatograph (AutoSystem GC, Perkin-Elmer) equipped with a thermal conductivity detector (TCD) and a stainless-steel 10′ x 1/8″ x .085″ HayeSep D 100/120 mesh (Alltech) packed column. The temperatures of column, injector, and detector were kept at 35, 60, and 150°C and argon gas was used as the carrier gas. The VFA composition and glycerine were analyzed by a high performance liquid chromatograph (HPLC, Aminex HPX-87H column) with a 4 mM H_2SO_4 mobile phase with ultraviolet (UV, 210 nm) and refractive index (RI) detectors. The influent and effluent COD values were analyzed by the dichromate method using a spectrophotometer (HACH DR 2700). Organic nitrogen was measured by the diazotization and cadmium reduction method and inorganic nitrogen was analyzed by the salicylate method. Total phosphorous was measured by the molybdovanadate method with acid persulphate digestion (Hach company). The mixed liquor volatile suspended solids (MLVSS) to represent the microbial concentration in bioreactor taken during the reaction step and volatile suspended

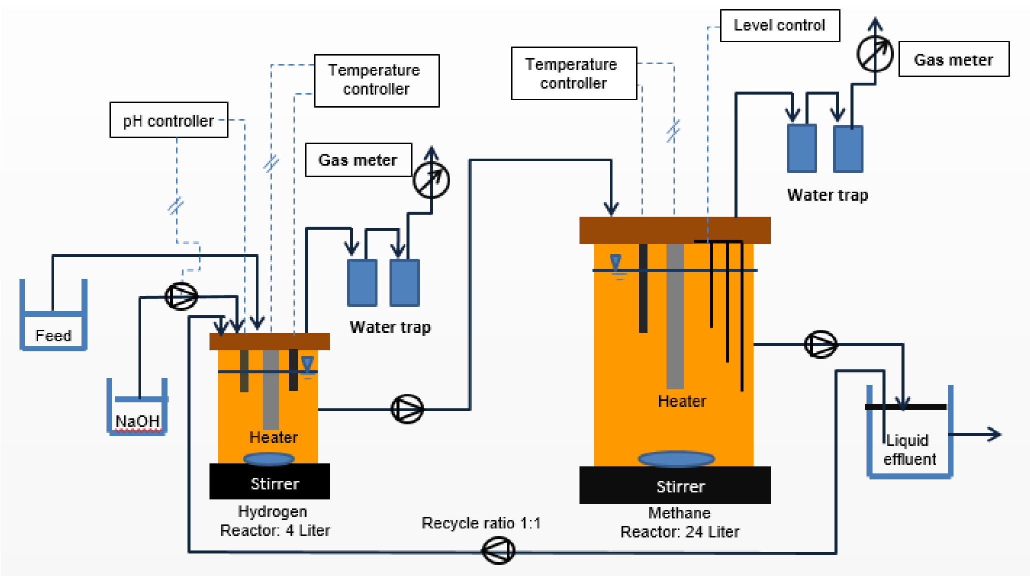

Figure 1: Schematic of two-stage anaerobic sequencing batch reactor (ASBR)

solids (VSS) to represent the microbial wash out from bioreactor taken during the decanting step were analyzed by the standard methods (Eaton et al., 2005).

3. Results and discussion

3.1 Hydrogen and methane production results

The produced gas from the hydrogen ASBR unit contained mainly hydrogen and carbon dioxide with a small amount of methane (Figure 2a). The percentage of hydrogen increased from 23.31 to 31.67 % with increasing COD loading rate from 33.75 to 67.50 kg/m^3 d and then decreased to 27.11% with further increasing COD loading rate up to 84.38 kg/m^3 d. The hydrogen production rate and specific hydrogen production rate (SHPR) had similar trends to the hydrogen content. The maximum hydrogen production rate (1.33 L/d) as shown in Figure 2a and SHPR (88.91 mL H_2/g MLVSS d or 332.54 mL H_2/L d) as shown in Figure 2c were found at COD loading rate of 67.50 kg/m^3 d. At a very high COD loading rate of 84.38 kg/m^3 d, the hydrogen production performance decreased because of the toxicity from volatile fatty acid (VFA) accumulation.

The produced gas from the methane ASBR unit contained mainly methane and carbon dioxide with a small amount of hydrogen (Figure 2b). The percentage of methane increased from 60.67 to 74.76 % with increasing COD loading rate from 5.63 to 11.25 kg/m^3 d and then decreased to 72.85 % with further increasing COD loading rate up to 14.06 kg/m^3 d. The methane production rate and specific methane production rate (SMPR) had similar trends to the methane content. The maximum of methane production rate (16.15 L/d) as shown in Figure 2b and SMPR (232.50 mL CH_4/g MLVSS d or 672.84 mL CH_4/L d) as shown in Figure 2d were found at a COD loading rate of 11.25 kg/m^3 d. At a very high COD loading rate of 14.06 kg/m^3 d, the methane production performance decreased.

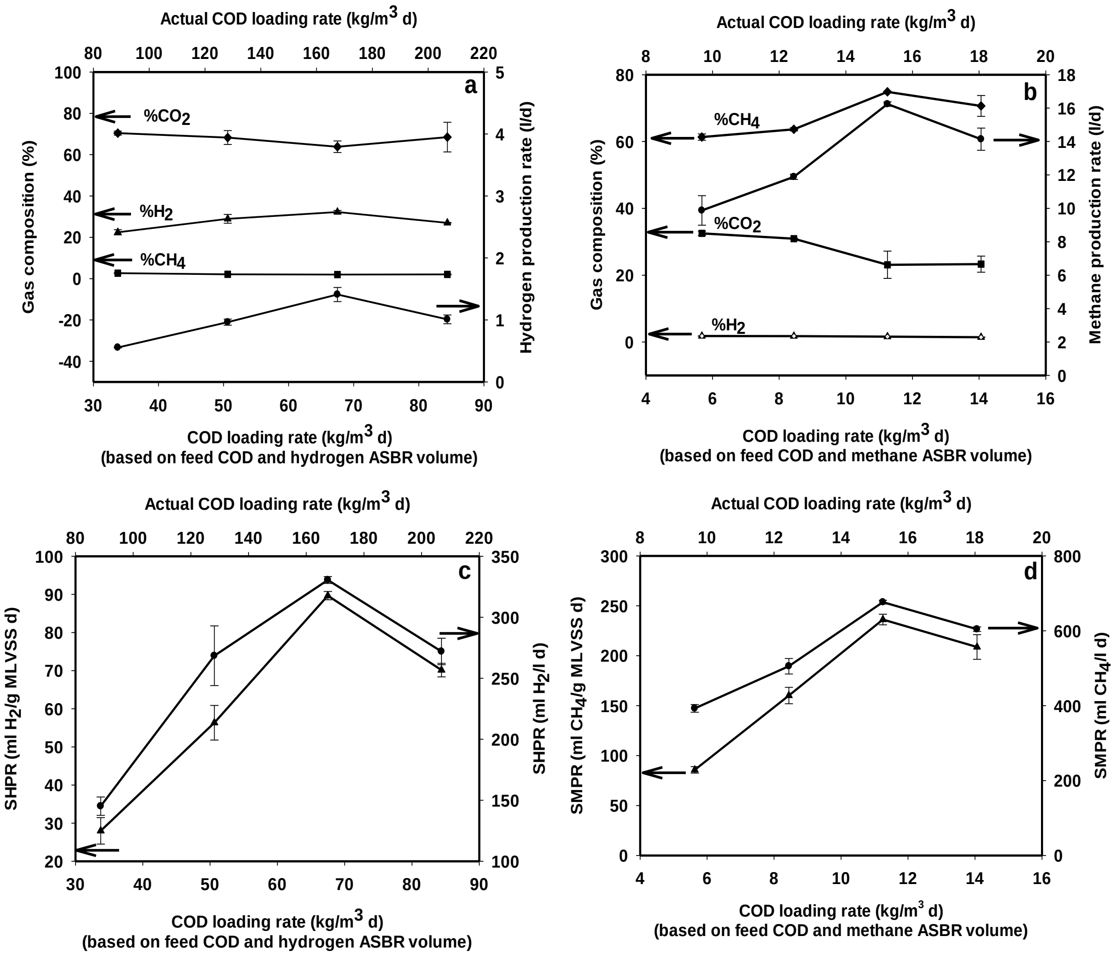

Figure 2: Effect of COD loading rate on (a) gas composition and hydrogen production rate, (b) gas composition and methane production rate, (c) specific hydrogen production rate, and (d) specific methane production rate

3.2 Volatile fatty acid (VFA) and 1,3-propanediol (1,3-PD) results

Figure 3a shows the effect of COD loading rate on total VFA concentration and its composition in the hydrogen ASBR unit. The main components of the VFA were propionic acid, acetic acid, butyric acid, and valeric acid with a small amount of 1,3-propanediol and a trace level of ethanol. The total VFA concentration increased with increasing COD loading rate and reached a maximum value at the highest COD loading of 84.38 kg/m^3 d. All components of the VFA had a similar trend to that of total VFA concentration. The two main organic acid components affecting hydrogen production performance are butyric acid (Arooj et al., 2008) and 1,3-propanediol (Sittijunda and Reungsang, 2012) according to Equations 3 and 5, respectively.

$$C_3H_8O_3 + H_2O \longrightarrow CH_3COOH + CO_2 + 3H_2 \qquad (1)$$
$$C_3H_8O_3 \longrightarrow CH_3CH_2COOH + H_2O \qquad (2)$$
$$2C_3H_8O_3 \longrightarrow CH_3CH_2CH_2COOH + 2CO_2 + 4H_2 \qquad (3)$$
$$C_3H_8O_3 \longrightarrow CH_3CH_2OH + CO_2 + H_2 \qquad (4)$$
$$C_3H_8O_3 + H_2 \longrightarrow C_3H_8O_2 + H_2O \qquad (5)$$

The total VFA concentration and its composition in the methane ASBR unit are shown in Figure 3b. The main component of VFA were acetic acid, propionic acid, butyric acid, and valeric acid with a significant concentration of 1,3-propanediol and a very small amount of ethanol. The total VFA concentration increased with increasing COD loading rate and reached the maximum value at the highest COD loading of 14.06 kg/m^3 d while methane production performance decreased due to high amount of organic acid formation and those organic acids could be accumulated in the system resulting in the reduction of pH. The concentration profile of any VFA had a similar trend to that of the total VFA concentration. Both organic acids and hydrogen are utilized by methanogens to generate methane according to the following equation (www.wtert.eu/default.com):

$$CH_3COOH \longrightarrow CH_4 + CO_2 \qquad (6)$$
$$CH_3CH_2CH_2COOH + 2H_2O \longrightarrow 2CH_3COOH + 2H_2 \qquad (7)$$
$$CH_3CH_2COOH + 2H_2O \longrightarrow CH_3COOH + CO_2 + 3H_2 \qquad (8)$$
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad (9)$$

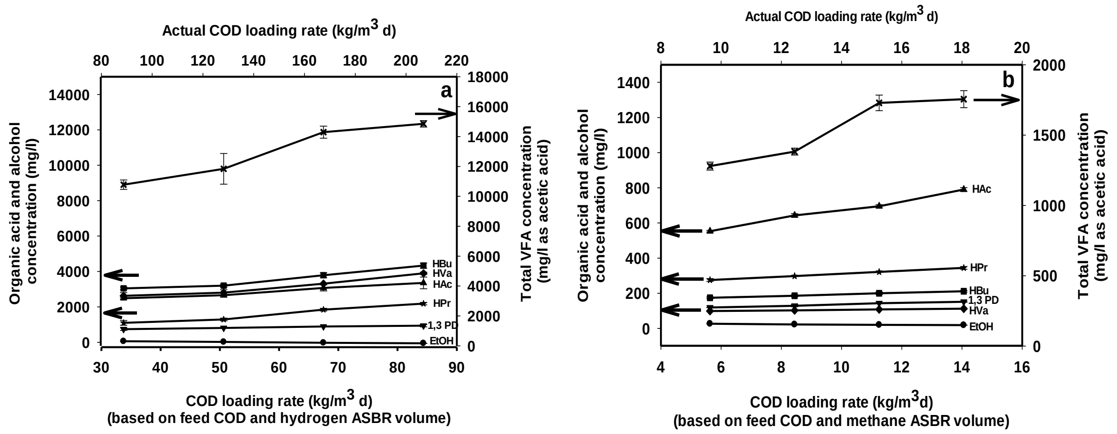

Figure 3: Effect of COD loading rate on total VFA, and VFA composition in (a) hydrogen ASBR unit (b) methane ASBR unit

3.3 Overall Performance

When the system was considered in one stage, the main compositions of produced gas were hydrogen, methane, and carbon dioxide (Figure 4a). The percentage of hydrogen and methane increased with increasing total COD loading rate from 4.82 to 9.64 kg/m^3 d and then decreased when further increasing total COD loading rate up to 12.05 kg/m^3 d. The maximum hydrogen percentage of 16.65% and the maximum methane percentage of 38.12 % were found at a total COD loading rate of 9.64 kg/m^3 d. Figure 4b shows specific hydrogen production rate (SHPR) and specific methane production rate (SMPR), the maximum SHPR and SMPR of 154 mL H_2/ L d and 355.00 mL CH_4/L d, respectively were found at a total COD loading rate of 9.64 kg/m^3 d. At a very high total COD loading rate of 12.05 kg/m^3 d, both SHPR and SMPR decreased due to the toxicity from volatile fatty acid (VFA) accumulation.

In addition, hydrogen yield (Figure 4c) and methane yield (Figure 4d) also indicated the hydrogen and methane production performance. The maximum value of hydrogen yield (34.19 mL H_2/g COD removed or 7.96 mL H_2/g COD applied) and the maximum value of methane yield (78.81 mL CH_4/g COD removed or 20.43 mL CH_4/g COD applied) were found at a total COD loading of 9.64 kg/m^3 d and then decreased when increasing total COD loading rate from 9.64 to 12.05 kg/m^3 d.

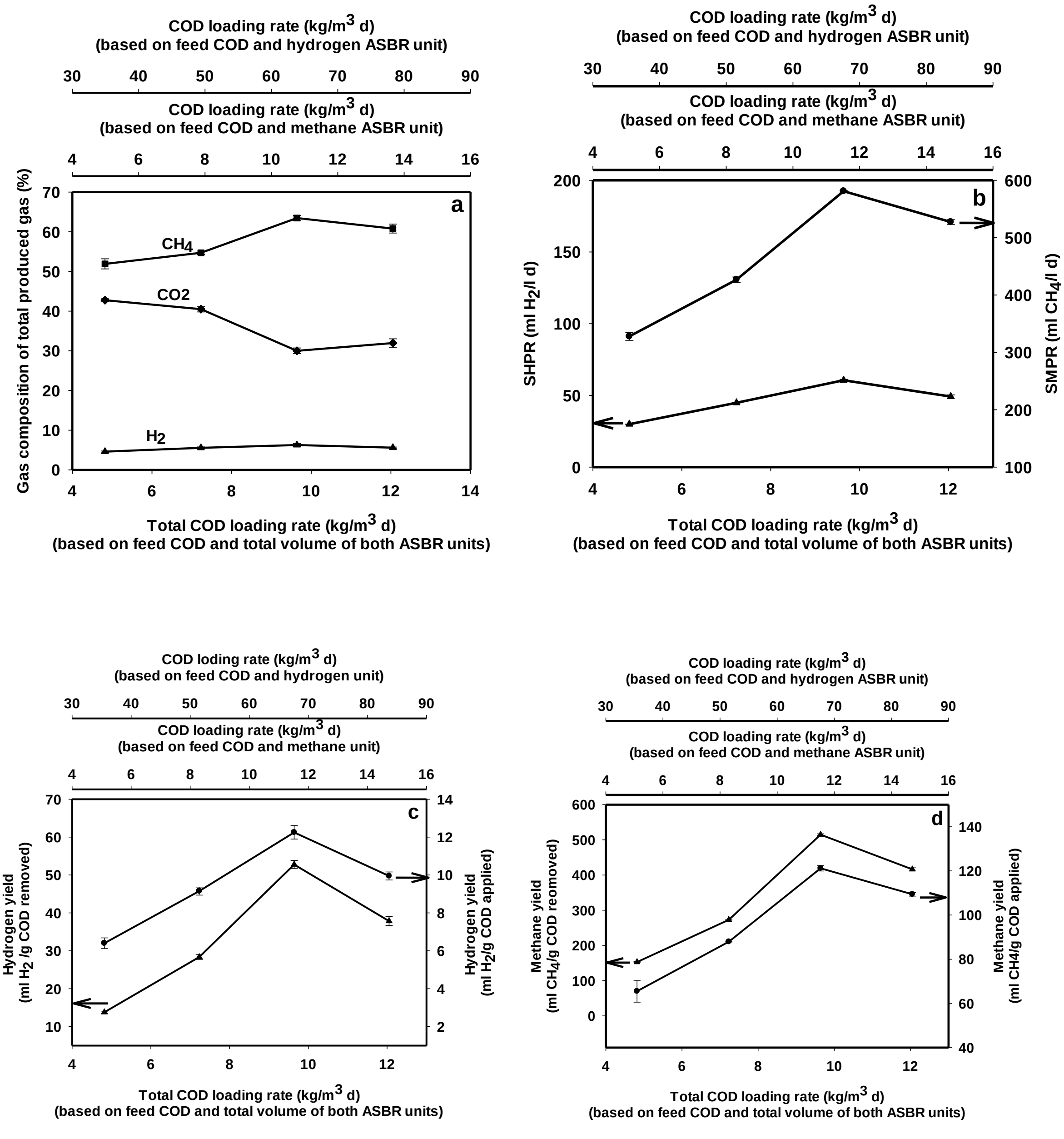

Figure 4: Effect of total COD loading rate on (a) gas composition, (b) specific hydrogen production rate (SHPR) and specific methane production rate (SMPR), (c) hydrogen yield and (d) methane yield.

4. Conclusion

The simultaneous production of hydrogen and methane from biodiesel wastewater was investigated by using two-stage ASBR system with 4 and 24 L of working volumes, respectively operated under mesophilic temperature (37 °C) with a recycle ratio of 1:1 in order to minimize NaOH consumption for pH control in the hydrogen ASBR unit. For the hydrogen ASBR unit was controlled at pH 5.5 and the optimum COD loading rate of 67.50 kg/m^3 d (based on hydrogen ASBR volume) which gave the maximum hydrogen performance in terms of the maximum hydrogen production rate (1.33 L/d), the maximum

hydrogen percentage (31.67 %), and the maximum specific hydrogen production rate, SHPR (88.91 mL H_2/g MLVSS d or 332.54 mL H_2/L d). For the methane ASBR unit operated without control pH, at the same optimum COD loading of 11.25 kg/m^3 d (based on methane ASBR volume), the system gave the maximum methane production performance in terms of the maximum methane production rate (16.15 L/d), the maximum methane percentage (74.76 %), and the maximum specific methane production rate, SMPR (233 mL CH_4/g MLVSS d or 672.84 mL CH_4/L d). However, at very high COD loading rate of 84.38 kg/m^3 d for hydrogen ASBR system and 14.06 kg/m^3 d for methane ASBR system, hydrogen and methane production performance decreased because of the toxicity of volatile fatty acid (VFA) accumulation in hydrogen reactor and methane reactor.
Moreover, the optimum total COD loading rate was found at a total COD loading rate of 9.64 kg/m^3 d which provided the highest total hydrogen and methane production performance in terms of the maximum hydrogen percentage (16.65 %) and maximum methane percentage (38.42 %), the maximum hydrogen yield (11.39 mL H_2/g COD removed or 2.65 mL H_2/ g COD applied) and maximum methane yield (26.27 mL CH_4/g COD removed or 6.11 mL CH_4/ g COD applied), and the maximum specific hydrogen production rate, SHPR (154 mL H_2/L d) and maximum specific methane production rate, SMPR (355.00 mL CH_4/L d).

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