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Simultaneous Production of Hydrogen and Methane from Cassava Wastewater Using a Two Stage Upflow Anaerobic Sludge Blanket System under Thermophilic Operation

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The objective of this study was to investigate the hydrogen and methane production from cassava wastewater by using a two stage upflow anaerobic sludge blanket (UASB) system under thermophillic operation (55 °C). The recycle ratio of the effluent from the methane bioreactor-to-the feed flow rate was fixed at 1:1 and the solution pH in the hydrogen bioreactor was maintained at 5.5 by a pH controller while the solution pH of the methane bioreactor was not controlled. The liquid working volumes of the hydrogen and methane bioreactors were 4 and 24 L, respectively. The two stage UASB system was operated at different COD loading rates (30, 60, 90, 120, and 150 kg/m^{3}d based on the hydrogen bioreactor volume). Under the optimum COD loading rate of 90 kg/m^{3}d based on the hydrogen bioreactor volume corresponding to 15 kg/m^{3}d based on the methane bioreactor volume for the hydrogen bioreactor, the produced gas contained 40 % H_2, 52 % CO_2 and 8 % CH_4 and the system provided a maximum hydrogen yield and specific hydrogen production rate of 18 mL/g COD removed and 520 mL/L d, respectively. Under this optimum COD loading rate, the produced gas of the methane bioreactor contained 65 % CH_4 and 35 % CO_2 without hydrogen and the system provided a maximum methane yield and specific methane production rate of 115 mL/g COD removed and 650 mL/L d, respectively. The operation of recycling from methane bioreactor to hydrogen bioreactor optimized the use of NaOH for pH control in the hydrogen production step.

1. Introduction

Biogas technology has been widely applied to several industrial wastewaters and animal wastes economically (Sirirote et al., 2010). It does not only produce combustible biogas which is widely used to substitute fuel oil for steam generation in industry but also reduces treatment cost. Several industrial wastewaters can be used to produce biogas such as cassava wastewater (Sreethawong et al., 2008), and alcohol wastewater (Show et al., 2012). In addition gaining the combustible biogas, anaerobic digestion has many advantages; for example, it can be operated at a high organic loading rate under ambient conditions, reduces the overall treatment cost, decreases the emission of greenhouse gases, and eliminates odorous problems. However, the anaerobic processes require a rather large size of bioreactor because of their slow rates. One of interesting techniques for the improvement of biogas production from wastewaters is a use of two-stage processes.

The two-stage process consists of two sequential steps of hydrogen and methane production units (Zhu et al., 2008). In the first unit, the organic compounds in wastewater are hydrolysed and converted anaerobically to hydrogen, carbon dioxide, and volatile fatty acids by acidogenic bacteria. Then, the effluent liquid from the first unit is continuously entered to the second unit to further produce methane by methanogenic bacteria. The two-stage anaerobic processes can produce a higher methane production rate and yield due to a better balance between the rates of volatile fatty acids production and consumption as compared to a single process (Xia et al., 2011). Sarada and Joseph (1996) reported that methane

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production efficiency of a two-stage anaerobic system operated at a temperature of 30 °C, a hydraulic retention time (HRT) of 24 d and an organic loading rate of 4.5 kg/m^3day gave 50 % increase in the gas production rate and 40 % increase in the methane yield when being compared with a single-stage process. In this research, hydrogen and methane productions from cassava wastewater were investigated by using a two-stage UASB process at a constant high temperature of 55 °C. The first hydrogen UASB unit was controlled at a constant pH 5.5. The liquid effluent from the hydrogen bioreactor was further fed to the methane UASB bioreactor to produce methane without pH control. The two-stage UASB unit was operated at different COD loading rates ranging from 5 to 25 kg/m^3d based on the methane UASB unit or 30 to 150 kg/m^3d based on the hydrogen UASB unit. The recycle ratio of liquid effluent flow rate from the methane UASB bioreactor-to-the feed flow rate was fixed at 1:1.

2. Materials and methods

2.1 Substrate preparation

The cassava wastewater used in this study was obtained from Ubon Bioethanol Co., Ltd., Ubon Ratchathani, Thailand. It was sieved to remove any large solid particles before use. The cassava wastewater used in the present work had a chemical oxygen demand (COD) value of 14,500 mg/L and a ratio of COD:nitrogen:phosphorous of 100:2.1:2.03, indicating that the studied cassava wastewater had sufficient amounts of both nutrients for anaerobic degradation (the theoretical ratio of COD:nitrogen:phosphorous is 100:1:0.4 for anaerobic decomposition for biogas production (Intanoo et al., 2012))

2.2 **UASB operation**

The upflow anaerobic sludge blanket (UASB) reactors used in the study were constructed from borosilicate glass with a 4 and 24 L working volume for hydrogen and methane UASB bioreactors, respectively. The temperatures inside both bioreactors were controlled constant at 55 ºC by circulating water through a water jacket of each bioreactor by a circulating/heating bath. The cassava wastewater was fed continuously to the bottom of the hydrogen UASB bioreactor (in upward direction) at any desired flow rate by using a peristaltic pump in order to obtain different COD loading rates (30, 60, 90, 120, and 150 kg/m^3d based on the hydrogen UASB working volume or 5, 10, 15, 20 and 25 kg/m^3d based on the methane UASB working volume). The pH of the hydrogen UASB unit was maintained at 5.5 by using a pH controller. The effluent from the hydrogen UASB unit was directly pumped into the methane UASB bioreactor by a peristaltic pump with a level control probe. The pH of the methane UASB unit was not controlled. In order to minimize the consumption of NaOH for the pH control of the hydrogen UASB unit, a recycle ratio of the methane UASB effluent flow rate-to-feed flow rate of 1:1 was used in this study. At any given COD loading rate, the two-stage UASB system was operated to reach steady state before taking effluent and produced gas samples for analysis and measurement. The steady state was justified when both of the gas production rates and the effluent COD values of both hydrogen and methane UASB units did not change with time.

2.3 Measurement and analytical methods

The volumes of produced gases from both UASB bioreactors were recorded daily by using wet gas meters (Ritter, TGO5/5). The compositions of both produced gas samples were determined by a gas chromatograph (Auto System GC, Perkin-Elmer) equipped with a thermal conductivity detector (TCD) and the analysis conditions were given elsewhere (Intanoo et al., 2012). The chemical oxygen demand values (COD) in the feed and effluent samples were quantified by using the dichromate method using a COD reactor and spectrophotometer (HACH, DR 2700). The amount of volatile fatty acid in mg as acetic acid per L was determined by the distillation-titration method (Eaton et al., 2005). The samples obtained from the steam distillation were also taken for the determination of organic acid compositions by using another gas chromatograph (PR 2100, Perichrom) equipped with a flame ionization detector (FID) and the analysis conditions were given elsewhere (Intanoo et al., 2012). The average values of all analyse and measurements (with less than 5 % standard deviation) were used to access the process performance of the two-stage UASB system.

3. Results and discussion

3.1 Hydrogen production performance results

The effect of COD loading rate on COD removal efficiency and gas production rate for the hydrogen UASB unit operated at 55 °C and pH 5.5 are shown in Figure 1a. Since the constant recycle ratio of 1:1 was used to operate the two-stage UASB system, an actual COD loading rate was also determined from the COD values of both feed and final effluent. The COD removal increased with increasing COD loading rate and attained a maximum value of 35 % at a COD loading rate of 90 kg/m^{3}d. The gas production rate also shows a similar trend to the COD removal. The maximum gas production rate (5.5 L/d) was found at the same COD loading rate of 90 kg/m^{3}d. The cassava wastewater had a high COD value of 14,500 mg/L. Hence a higher COD loading rate simply provided a higher organic compound which was available for microbial activity, leading to both increases in COD removed and gas production rate. On the other hand, when COD loading rate increased from 90 to 150 kg/m^{3}d, the decreases in both COD removal and gas production rate resulted from the increasing toxicity from organic acid accumulation which will be discussed latter.

The gas composition and hydrogen production rate of the hydrogen UASB unit as a function of COD loading rate are shown in Figure 1b. The produced gas of the hydrogen UASB bioreactor mainly contained hydrogen and carbon dioxide with a small amount of methane. The methane content decreased steadily with increasing COD loading rate, corresponding to a reduction of hydraulic retention time (HRT) from 12 at a COD loading rate of 30 kg/m^{3}d to 2.4 h at a COD loading rate of 150 kg/m^{3}d (Solera et al., 2002). The hydrogen content increased with increasing COD loading rate from 30 to 90 kg/m^{3}d and then decreased with further increasing COD loading rate from 90 to 150 kg/m^{3}d. The maximum values of both hydrogen content and hydrogen production rate were 40 % and 2.2 L/d, respectively. The first increase in hydrogen production rate with increasing hydrogen content resulted from the increase in organic loading available for the microbial activity. However, the decreases in hydrogen production rate and content with further increasing COD loading rate from 90 to 150 kg/m^{3}d resulted from the increasing toxicity from increasing VFA in the system, as mentioned before (Luo et al., 2010). The CO_2 concentration of the produced gas showed an opposite trend to the H_2 concentration.

The specific hydrogen production rate (SHPR) represented the ability of microbes to produce hydrogen from organics per unit volume of reactor or per unit weight of microbes, in which are very useful for scaling up a bioreactor. Both SHPR values increased with increasing COD loading rate from 30 to 90 kg/m^{3}d and then decreased with further increasing COD loading rate from 90 to 150 kg/m^{3}d (Figure 1c). Both maximum SHPR values found at the COD loading rate of 90 kg/m^{3}d were 22 mL H_2/g MLVSS d and 530 mL H_2/L d which were consistent with the maximum values of hydrogen production rate, hydrogen content, and COD removal.

In addition, hydrogen yield represented the efficiency of conversion of organic compounds to hydrogen by microbes in terms of mL H_2/g COD applied or mL H_2/g COD removed was also determined in this study. They showed the similar trend to SHPR (Figures 1c-d). The maximum hydrogen yield of 18 mL H_2/g COD removed (or 11 mL H_2/g COD applied) was found at a COD loading rate of 90 kg/m^{3}d which corresponded to the highest SHPR and hydrogen production performance. The higher hydrogen production efficiency resulted from the higher organic compounds loading to the system to provide more food for the microorganisms to produce more hydrogen. Again, the SHPR and hydrogen yield sharply decreased when the COD loading rate beyond 90 kg/m^{3}d due to the toxicity from the VFA accumulation.

3.2 Methane production performance results

As described before, the liquid effluent from the hydrogen UASB unit was directly fed to the methane UASB unit for further producing methane. The methane bioreactor was also operated under thermophilic temperature (55 °C) without pH control. Figure 2a shows the COD removal at different COD loading rates (based on either feed COD or the actual incoming COD). The COD removal increased with increasing COD loading rate and reached a maximum value of 72 % at a COD loading rate of 15 kg/m^{3}d (based on feed COD and the methane UASB volume). Beyond the optimum COD loading rate of 15 kg/m^{3}d, the COD removal slightly decreased with further increasing COD loading rate. The gas production rate showed a similar trend to the COD removal. Interestingly, the gas production rate of the methane UASB unit was about 4 times higher than that of hydrogen UASB unit, corresponding to the sizes of both bioreactors.

The composition of produced gas from the methane UASB unit mainly contained methane and carbon dioxide with a very small amount of hydrogen (less than 0.5 %) (Figure 2). Both methane content and methane production rate increased with increasing COD loading rate from 5 to 15 kg/m^{3}d but they decreased with further increasing COD loading rate from 15 to 25 kg/m^{3}d (Figure 2b). In contrast, the CO_2 content in the produced gas showed an opposite trend. The maximum methane content and methane production rate of 68 % and 16 L/d, respectively were found at a COD loading rate of 15 kg/m^{3}d, corresponding to the optimum COD loading rate of 90 kg/m^{3}d (based on COD feed and the hydrogen UASB volume) for the maximum hydrogen production performance.

Figure 2c-d shows the specific methane production rates (SMPR) and methane yields, as a function of COD loading rate. They increased with increasing COD loading rate and then decreased with further increasing COD loading rate from 15 to 25 kg/m^{3}d. The maximum SMPR (650 mL CH_4/l d or 45 mL CH_4/g MLVSS d) and methane yield (107 mL CH_4/g COD removed or 42 mL CH_4/g COD applied) were found at a

COD loading rate of 15 kg/m^{3}d. Hence, the COD loading rate of 15 kg/m^{3}d was considered to be an optimum organic loading rate for both production of hydrogen and methane by two-stage UASB unit.

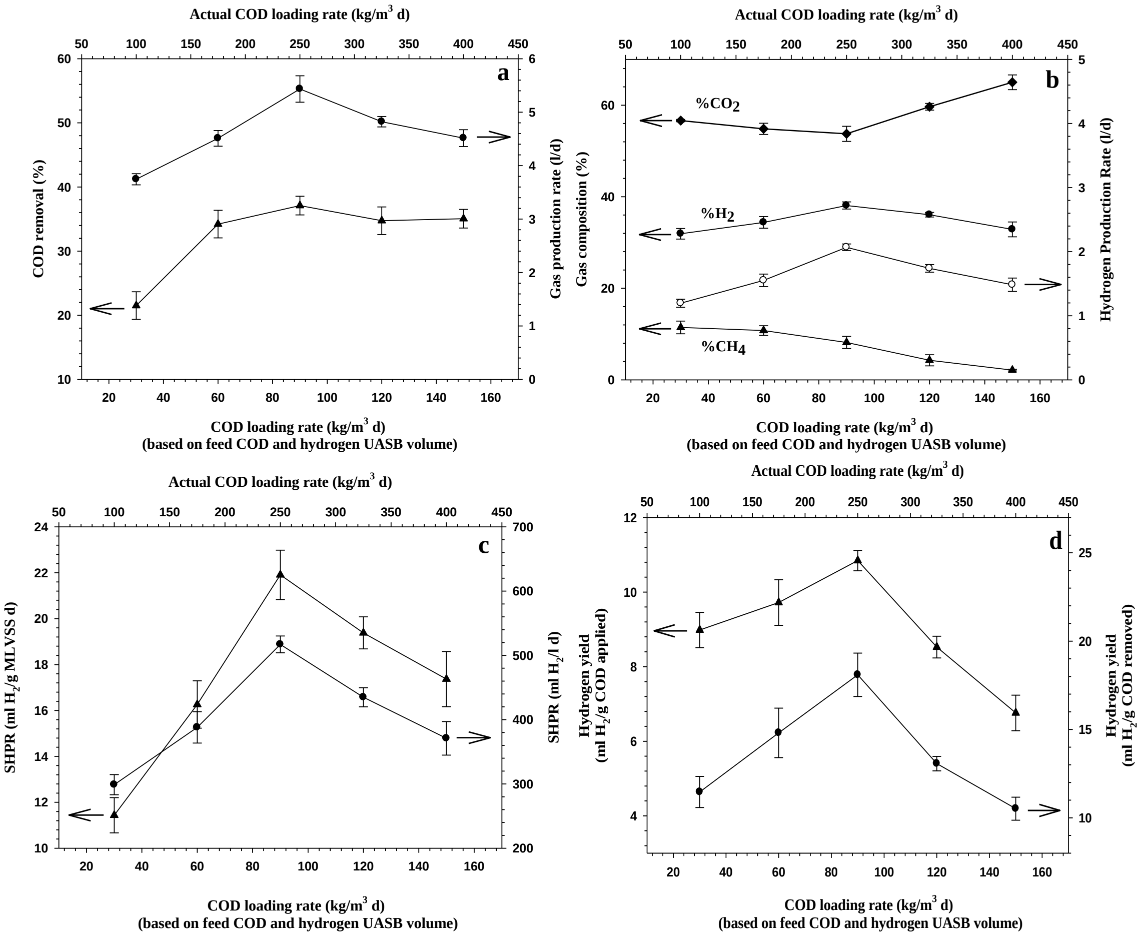

Figure 1: Effects of COD loading rate on (a) COD removal and gas production rate, (b) gas composition and hydrogen production rate, (c) specific hydrogen production rates and (d) hydrogen yield of the hydrogen UASB unit

3.3 Volatile fatty acid (VFA) and VFA composition

The effects of COD loading rate on total VFA concentration and VFA composition in the hydrogen and methane UASB unit are shown in Figure 3. The total VFA concentration increased markedly with increasing COD loading rate from 30 to 120 kg/m^{3}d in hydrogen UASB unit and from 5 to 25 kg/m^{3}d in methane UASB unit but it slightly increased with further increasing COD loading rate beyond 120 and 15 kg/m^{3}d, respectively. The maximum total VFAs concentration (16,000 and 780 mg/L as acetic acid) was found at the highest COD loading rate of 150 kg/m^{3}d in hydrogen UASB unit and 25 kg/m^{3}d in methane UASB unit. As compared the results shown in Figures 3, it can be concluded that the toxic level of VFA was around 10,000 and 400 mg/L as acetic acid for the cassava wastewater under the studied conditions to the hydrogen and methane-producing bacteria which is consistent to our previous studies (Intanoo et al., 2012).

Under hydrogen production system, the main components of VFA are acetic acid (HAc), propionic acid (HPr), butyric acid (HBu), and valeric acid (HVa). All produced organic acids had a similar trend to that of the total VFA concentration except the propionic acid concentration slightly increased with increasing COD loading rate. The butyric acid concentration was the highest while propionic acid concentration was the lowest (Hawkes et al., 2002), in which contributed to the system having high hydrogen production performance (Wang et al., 2009).

Under methane production system, the main components of VFA are acetic acid (HAc), propionic acid (HPr), butyric acid (HBu), and valeric acid (HVa). At any given COD loading, the concentration of acetic acid was the highest followed by propionic acid, butyric acid, and valeric acid, respectively. The highest acetic acid concentration resulted from the further degradation of both propionic acid and butyric acid, according to equation 1-2 (Abbasi et al., 2012). The production of methane mainly resulted from the two basic bioconversion reaction of hydrogenotrophic and acetotrophic, as shown in Eq(3) and Eq(4) (Abbasi et al., 2012).

$$CH_3CH_2CH_2COOH + 2H_2O \longrightarrow 2CH_3COOH + 2H_2 \quad (1)$$
$$CH_3CH_2COOH + 2H_2O \longrightarrow CH_3COOH + CO_2 + 3H_2 \quad (2)$$
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad (3)$$
$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad (4)$$

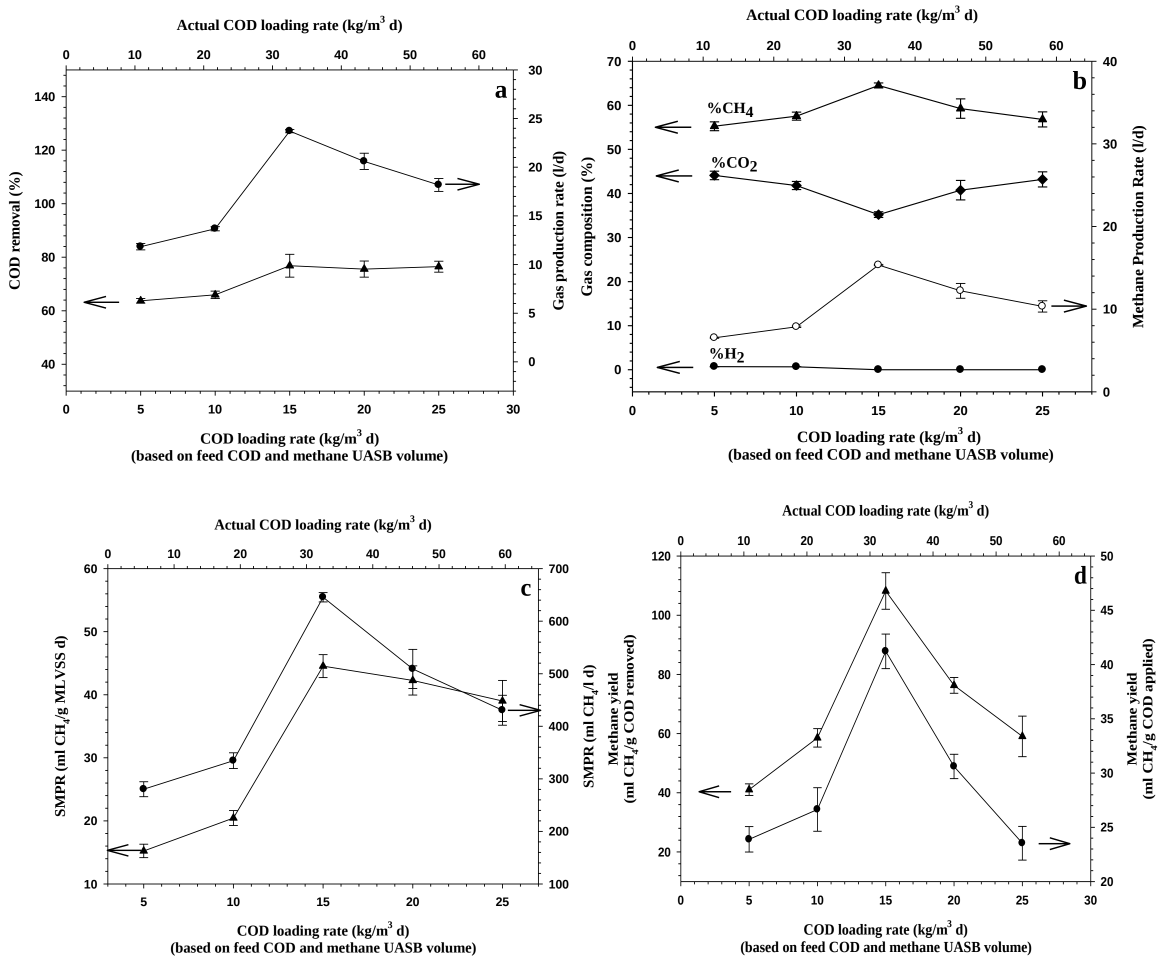

Figure 2: Effects of COD loading rate on (a) COD removal and gas production rate, (b) gas composition and methane production rate, (c) specific methane production rates and (d) methane yield of the methane UASB unit

4. Conclusions

Hydrogen and methane production from cassava wastewater under thermophilic (55 °C) two-stage upflow anaerobic sludge blanket reactor (UASB) process. The first hydrogen production process was operated at a constant pH of 5.5. The highest hydrogen production performance provided the highest hydrogen percentage (40 %), the highest hydrogen production rate (2.2 L/d), the highest hydrogen yield (11 mL H_2/g COD applied) and the highest SHPR (22 mL H_2/g MLVSS d) which corresponded to the highest COD removal efficiency (35 %), high butyric acid concentration (4,000 mg/L), and the lowest propionic acid (1,200 mg/L) was found at COD loading rate of 90 kg/m^{3}d. For the second methane production process, the system was operated without pH controlled. At a COD loading rate of 15 kg/m^{3}d, the highest methane percentage (68 %), the highest methane production rate (16 L/d), the highest methane yield (42 mL CH_4/g COD applied), and the highest SMPR (45 mL CH_4/g MLVSS d) were obtained consistence with the highest COD removal efficiency (72 %), and the highest acetic concentration (175 mg/L). At a COD loading rate of 90 kg/m^{3}d was considerable optimum organic compound loading for hydrogen production process and a COD loading rate of 15 kg/m^{3}d was an optimum organic loading for methane production process. The different concentration of sodium in feed and the final effluent were not significantly different, indicating that the operation of effluent recycle could minimize the consumption of NaOH for the pH adjustment in the hydrogen production step.

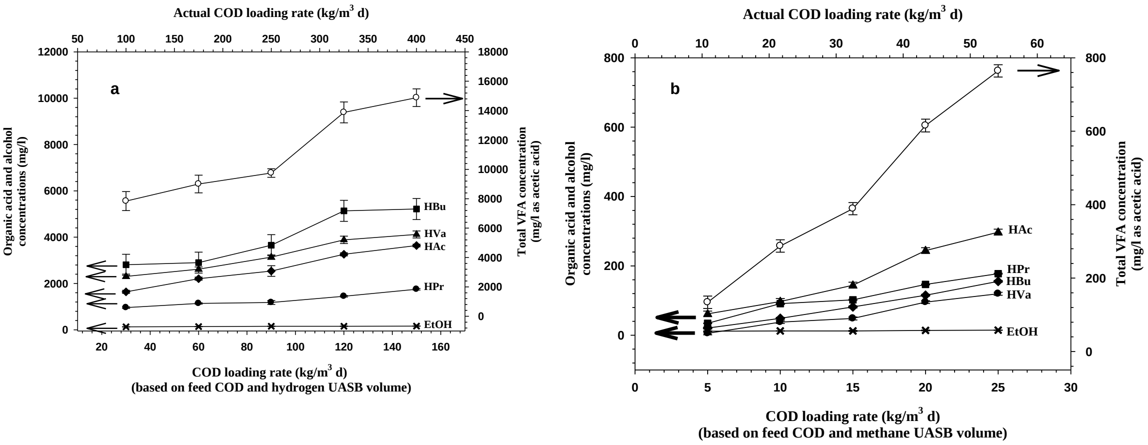

Figure 3 Total VFA, and VFA composition versus COD loading rate of (a) the hydrogen UASB unit, (b) the methane UASB unit

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