Organics removal and biogas production characteristics of UASB in treating sulfate-rich wastewater

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Abstract

To find an appropriate method for wastewater containing ethanol and acetate with COD/sulfate ratio of 1, a UASB reactor with granular sludge was operated more than 180 days. The results indicated that this system removed more than 80% of COD and 30% of sulfate with HRT (hydraulic retention time) above 6 h and OLR (organic loading rate) below 12.3 gCOD/L d. Further HRT decrease caused volatile fatty acids accumulation. At HRT of 2 h, free sulfide increased above 110 mg/L, and resulted in COD removal deterioration. Methane-producing bacteria (MPB) always predominated over SRB (sulfate-reducing bacteria) in organics utilization. Except for the HRT of 2 h, methane accounted for 70-80% in the biogas and methane yield kept in the range of 0.18-0.24 LCH_4/gCOD.

Keywords

sulfate-rich; UASB; biogas; methane-producing bacteria (MPB); sulfate-reducing bacteria (SRB)

INTRODUCTION

Although there have been some researches on sulfate reduction with ethanol and acetate as carbon sources. Most of them focused on how to improve sulfate removal with different kinds of substrates or how to enhance heavy metals removal with sulfide formation during sulfate reduction. Few studies were concerned with how to promote organics removal and methane production in high sulfate situation. Moreover, ethanol is often taken as an excellent substrate for sulfate reduction. In the presence of ethanol in sulfate-rich wastewater, sulfidogenesis always takes predominance in anaerobic digestion, resulting in acetate accumulation and low methane production.

In this research, a UASB had been run over 180 days to treat sulfate-rich wastewater with COD/sulfate ratio of 1. This reactor had shown high performance in organics removal and methane production.

MATERIAL AND METHODS

Experimental setup

The UASB reactor is shown in Fig. 1. This reactor was made of cylinder organic glass, and had a reacting zone with height of 0.8 m and volume of 6 L. It was run at 35±1 ºC with heated water recirculation from a water circulation heater. This reactor was inoculated on Oct. 10, 2011, with 3 L mesophilic granular sludge from a full-scale UASB reactor treating food manufacturing wastewater in Miyagi of Japan.

Wastewater composition

According to the composition of the real wastewater in a chemistry plant, synthetic wastewater was made in laboratory. This wastewater mainly contained about 1000 mg/L acetate, 1000 mg/L ethanol, 3000 mg/L sulfate, and had COD/sulfate ratio of about 1. Sodium sulfate was used to supply sulfate in the wastewater.

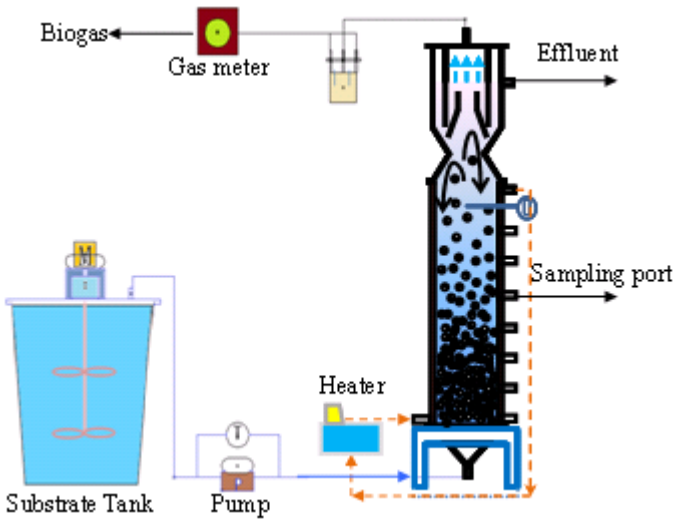

Figure 1. Schematic diagram of the granular sludge UASB

Chemical analysis

COD, sulfate, dissolved sulfide and total sulfide were measured with standard methods according to the APHA standard method. Free sulfide (undissociated H_2S) in the water was calculated by the first stage ionization equilibrium of hydrogen sulfide. Acetate, ethanol and other volatile fatty acids (VFA) were analyzed by gas chromatography (GC, Agilent 6890). CH_4 and H_2S in the biogas were determined with gas chromatography (SHIMADZU GC-8) and hydrogen sulfide detecting tubes (Gastec, No. 4H), respectively.

RESULTS AND DISCUSSION

Organics removal performance

As shown in Fig. 2 (a) and Fig. 3 (a), with HRT decreasing gradually from 48 h to 2 h, OLR increased from 1.4 gCOD/L d to 37.8 gCOD/L d. With HRT above 6 h and OLR below 12.3 gCOD/L d, COD removal rate was steadily maintained in the range of 86.5-90.9%. When OLR was further increased with HRT reduction, COD removal rate decreased greatly. At OLR of 37.8 gCOD/L d with HRT of 2 h, only about 42% of COD was removed. It can also be noticed that organic removal rate (ORR) increased linearly with OLR below 12.3 gCOD/L d. After that the increase rate of ORR slowed down, and ORR attained the highest value of 17.8 gCOD/L d at OLR of 24.7 gCOD/L d. There was an obvious increase of VFA in the effluent accompanying with HRT reduction and OLR increase (Fig. 2 (b)). At HRT of 6 h, VFA in the effluent was below 360 mg/L. At HRT of 3 h and 2 h, VFA in the effluent rose above 520 mg/L and 870 mg/L, respectively. The highest VFA reached around 1120 mg /L at HRT of 2 h. Apparently, VFA accumulation happened in the reactor. The high VFA in the effluent resulted in organics removal deterioration. However, there was no ethanol detected in the effluent at all HRTs, which indicated ethanol was decomposed or converted completely. Acetate removal in anaerobic digestion is usually the limiting step in COD removal. As the HRT was adjusted back to 6 h from Day 135, VFA in the effluent decreased gradually. After 10 days of recovery, VFA decreased below 400 mg/L (acetate) and this system regained COD removal rate above 80%.

Sulfate removal and sulfide variation

Although COD removal changed greatly with HRT reduction, sulfate removal was relatively stable. As shown in Fig. 2 (c), with HRT below 6 h, the effluent sulfate was always around 2000 mg/L with sulfate removal ratio around 30%. There was no evidence for sulfate removal increase with time extension. SRB usually competes effectively at low substrate levels. At HRT of 6 h, there was still above 350 mg/L of COD left in the effluent of this UASB (Fig. 2 (a)), and SRB could not take predominance at such high substrate levels.

With HRT below 6 h, total sulfide and dissolved sulfide concentration in the effluent kept stably around 250-300 mg/L and 220-290 mg/L, respectively (Fig. 2 (d)). However, free sulfide concentration fluctuated

greatly especially with HRT below 3 h. At HRT of 2 h, free sulfide concentration increased above 110 mg/L. Gaseous and dissolved sulfides usually cause physical-chemical and biological constraints in anaerobic digestion, which may lead to process failure. The thresholds for digestion inhibition are in wide and confusing ranges of 150-1100 mg/L for dissolved sulfide and 50-250 mg/L for free sulfide. In this research, although free sulfide increased greatly to 110-123 mg/L at HRT of 2 h, at other HRTs, dissolved sulfide and free sulfide fluctuated in the ranges of 180-290 mg/L and 10-80 mg/L, respectively. Except for the HRT of 2 h, there was no signal of digestion inhibition by dissolved sulfide and free sulfide. Moreover, although COD removal decreased greatly at HRT of 2 h, sulfate removal was hardly affected. Maybe the free sulfide over 110 mg/L caused inhibition to methanogenesis, but had little influence on sulfidogenesis in this UASB.

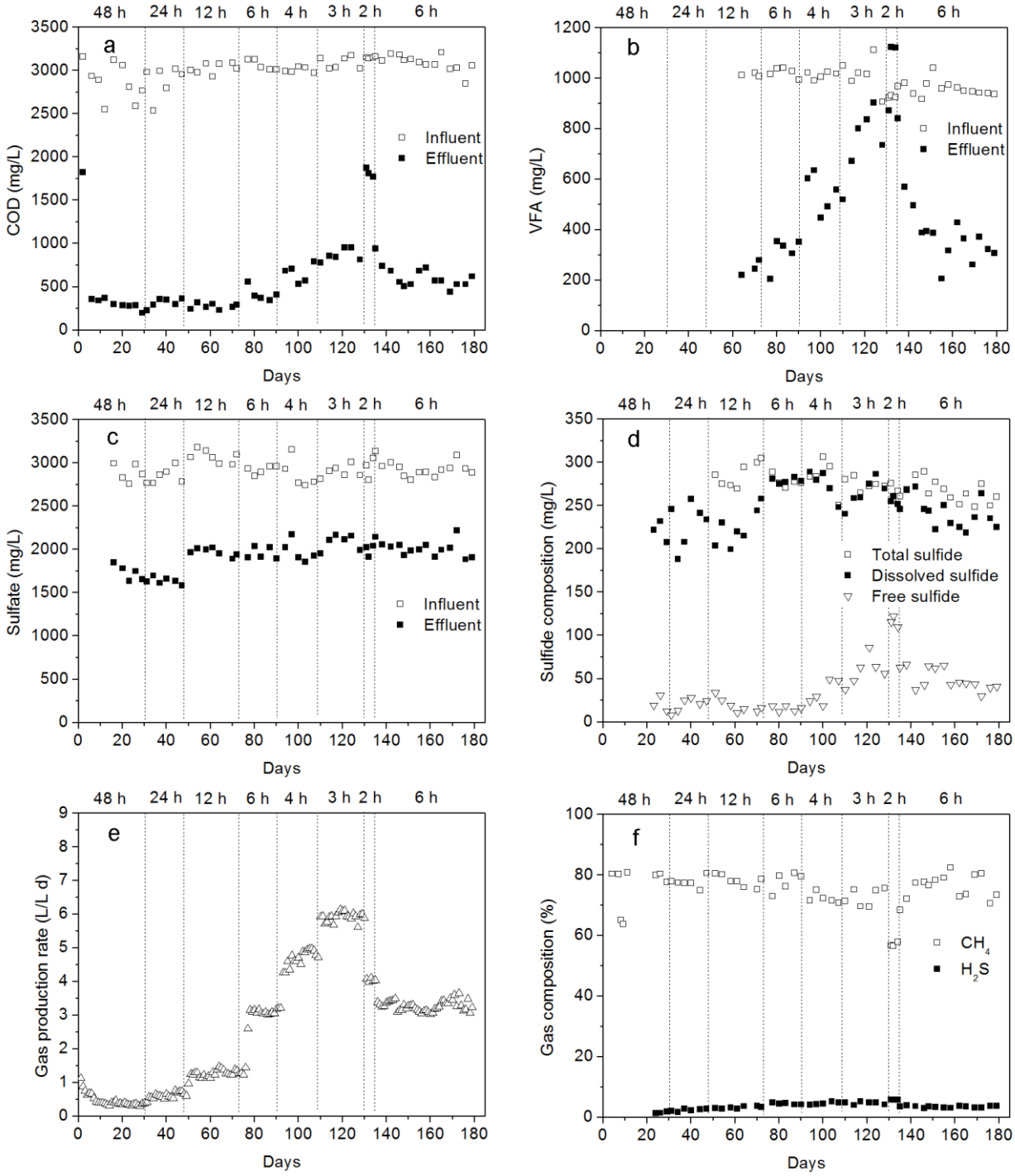

Figure 2. The overall performance: (a) COD; (b) VFA; (c) sulfate; (d) sulfide; (e) gas production; (f) gas composition.

Gas production performance

The gas production rate was affected greatly with HRT decrease (Fig. 2 (e)). The average gas production rate was only 0.37 L/L d at HRT of 48 h. With HRT decreasing gradually, gas production rate increased to 5.92 L/L d at HRT of 3 h. At HRT of 2 h, owing to the acidification of the reactor, methanogenesis was inhibited greatly and gas production rate then declined to 4.05 L/L d.

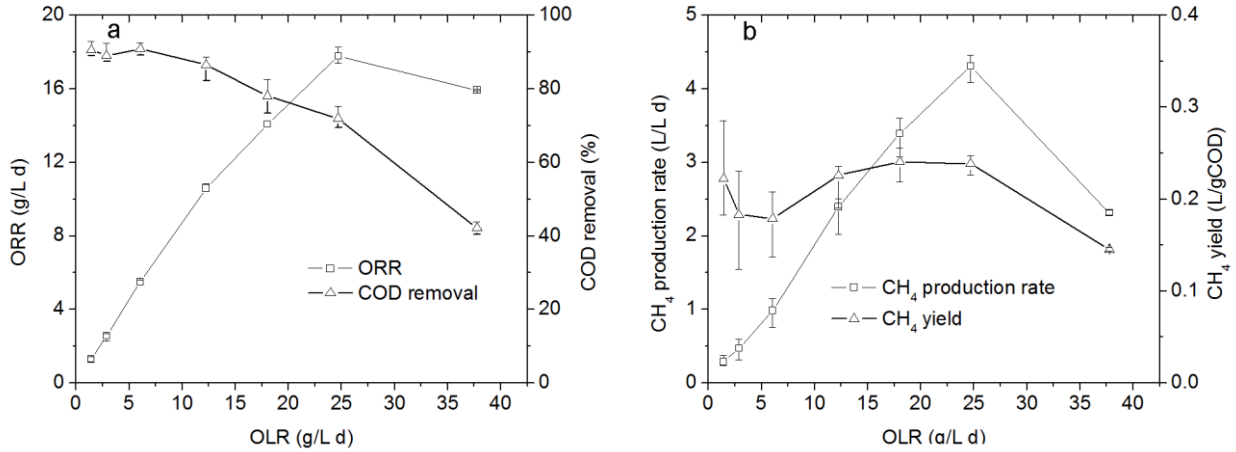

Figure 3. OLR variation on COD removal and methane production: (a) COD; (b) methane production.

Except for the starting-up period and HRT of 2 h operation, methane percentage in the biogas kept mostly in the range of 70-80% (Fig. 2 (f)). Accompanying with the increase of VFA level in the reactor during HRT reduction, there was a descending trend of methane content in the biogas. With HRT above 6 h, methane percentage kept around 80%. In this UASB, methane was always the main component in the biogas, which indicated methane production by MPB predominated in this UASB.

According to gas production and composition at all HRTs, the methane production rate (L/L d) and methane yield (L/gCOD) at different OLRs was obtained and showed in Fig. 3 (b). Methane production rate increased from 0.29 L/L d to 4.31 L/L d with OLR changing from 1.4 gCOD/L d to 24.7 gCOD/L d, then decreased to 2.31 L/L d at OLR of 37.8 gCOD/L d. However, there was no much change in methane yield. The lowest value of 0.15 L/gCOD was seen at OLR of 37.8 gCOD/L d. At other OLRs, methane yield kept in the range of 0.18-0.24 L/gCOD. At OLR of 12.3 gCOD/L d with HRT of 6 h, this reactor got a methane yield of 0.23 L/gCOD. Although the methane yield in this study was lower than the theoretical methane yield of 0.35 LCH_4/gCOD, it was much higher than that in other studies with low COD/sulfate ratios.

CONCLUSION

With HRT above 6 h and OLR below 12.3 gCOD/L d, this UASB removed more than 80% of COD, and no ethanol was left in the effluent. Free sulfide concentration increased above 110 mg/L at HRT of 2 h, and caused digestion inhibition to organics removal. Methane production by MPB predominated in this UASB, and methane content maintained 70-80% in the biogas. Except for this HRT, this system got methane yield in the range of 0.18-0.24 L/gCOD.

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