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UASB performance and electron competition between methane-producing archaea and sulfate-reducing bacteria in treating sulfate-rich wastewater containing ethanol and acetate

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HIGHLIGHTS

- MPA predominated in COD and electrons utilization in high sulfate situation.
- At HRT of 6 h, methane yield reached 0.23 L/gCOD with COD removal above 80%.
- Methane was generated by *Methanosaeta concilii GP6* with acetate as substrate.
- Sulfate was mainly reduced by *Desulfovibrio* species with ethanol as substrate.
- SRB accounted for 17.6% in bacteria and all belonged to incomplete oxidizers.

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ABSTRACT

To find an appropriate method for sulfate-rich wastewater containing ethanol and acetate with COD/sulfate ratio of 1, a UASB reactor was operated for more than 180 days. The influences of HRT (hydraulic retention time) and OLR (organic loading rate) on organics and sulfate removal, gas production, and electrons utilization were investigated. The sludge activity and microorganism composition were also determined. The results indicated that this system removed more than 80% of COD and 30% of sulfate with HRT above 6 h and OLR below 12.3 gCOD/L d. Further HRT decrease caused volatile fatty acids accumulation and performance deterioration. Except at HRT of 2 h, COD and electron flow were mostly utilized by methane-producing archaea (MPA), and methane yield remained in the range of 0.18–0.24 LCH_4/gCOD. Methane was mainly generated by *Methanosaeta concilii GP6* with acetate as substrate, whereas sulfate was mainly reduced by incomplete-oxidizing *Desulfovibrio* species with ethanol as substrate.

1. Introduction

Anaerobic digestion is widely utilized especially in high strength organic wastewater treatment since it is both cost-effective and environmentally safe. There are many anaerobic digestion processes for sulfate-rich wastewater treatment such as UASB (Lens et al., 1998), expanded granular sludge bed (Dries et al., 1998), membrane reactor (Vallero et al., 2005) and anaerobic fluidized-bed reactor (Kaksonen et al., 2003). These processes are usually efficient in organics removal and methane production with low sulfate concentration. However, the presence of high sulfate in wastewater can cause significant problems resulting from sulfate reduction (Mizuno et al., 1998). In anaerobic treatment processes, SRB (sulfate-reducing bacteria) and MPA (methane-producing archaea, in many literatures called as methane-producing bacteria) always compete for carbon source (Acharya et al., 2008). In sulfate-rich wastewater digestion, SRB often outcompete MPA, and produce corrosive and poisonous sulfide during sulfate reduction (Xu et al., 2012). High level of sulfide is toxic to both MPA and SRB. Its accumulation in the digestion reactors usually causes inhibition effects on organics removal and methane production, and can even result in system failure. Moreover, large quantities of sulfide formation can affect biogas quantity and quality. Consequently, there have been many studies on alleviating the influence of sulfide in anaerobic digestion by using sulfide removal steps and processes, and some researchers have searched for appropriate methods to suppress sulfate reduction and improve organics removal in anaerobic reactors (Aboutalebi et al., 2012).

SRB are anaerobic microorganisms that employ sulfate as an electron acceptor to produce hydrogen sulfide. According to the

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completeness of organics biodegradation during sulfate reduction, SRB are usually classified into two categories: complete oxidizing SRB and incomplete oxidizing SRB. The competition between SRB and MPA in digestion depends largely on the types of substrates and COD/sulfate ratio (Li et al., 1996). SRB can utilize many low molecular weight compounds including butyrate, lactate, propionate, acetate, ethanol and methanol (Nagpal et al., 2000). Normally, SRB have an advantage over MPA during such substrates utilization due to their favorable kinetic properties and thermodynamic conditions (Mizuno et al., 1998). In low COD/sulfate situation, SRB always predominate in carbon source utilization and electron flow transmission, and suppress the activity of MPA (Shin et al., 1997). In a study with ethanol, lactate and glycerol as substrates for anaerobic sulfate reduction, no methane production was observed (Dinkel et al., 2010). In a horizontal-flow anaerobic reactor treating sulfate-rich wastewater with ethanol, acetate, propionate and butyrate as carbon sources, Damianovic and Foresti (2007) found that sulfidogenesis predominated in organics removal and no methane was detected in the biogas.

Although there have been some researches on sulfate reduction with ethanol and acetate as carbon sources, most of them have been focused on how to improve sulfate removal and how to enhance heavy metals removal with sulfide formation during sulfate reduction. Few studies have been done on how to promote organics removal and methane production in high sulfate situation. Ethanol is often considered as an excellent substrate for sulfate reduction since sulfidogenesis always takes predominance in the presence of ethanol in sulfate-rich wastewater digestion. This usually results in acetate accumulation and low methane production. In this research, to find an appropriate method for wastewater containing about 3000 mg/L of sulfate (SO_4^{2-}), 1000 mg/L of ethanol and 1000 mg/L of acetate (about 3000 mg/L of COD in total), a UASB reactor had been run for more than 180 days. The performance of this reactor in COD and sulfate removal, sulfide formation and gas production under different HRT (hydraulic retention time) and OLR (organic loading rate) was studied. The balance of COD and sulfate conversion during digestion was also investigated. According to methane and sulfide production in this reactor, the competition between MPA and SRB in electron flow utilization at different HRT was analyzed. To elucidate the pathways of COD and sulfate removal and conversion, SMA (specific methanogenic activity) and SSA (specific sulfidogenic activity) of the granular sludge in this reactor were determined with batch experiments, and the composition of microorganisms was analyzed with gene cloning method. These results were used to clarify the main digestion pathways of ethanol and acetate. This reactor had shown high performance with regard to both organics removal and methane production.

2. Methods

2.1. Reactor

The UASB reactor used in this study is shown in Fig. 1. This reactor was made of organic glass with an internal diameter of 100 mm. It had a reacting zone with height of 0.8 m and volume of 6 L. The wastewater was pumped from an influent tank with effective volume of 70 L. Heated water was supplied with a water circulation heater to the outer layer of the reactor to keep this reactor with relatively stable temperature of 35 ± 1 °C.

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, Japan. With a starting-up HRT of 48 h, more than 85% of COD was removed after 15 days operation. The granular sludge was kept well during the whole operation, and the average diameter and sedimentation velocity of the granules were about 1.8 mm and 96.5 m/h, respectively.

2.2. Wastewater composition

This research was done to study the feasibility of anaerobic treatment to actual wastewater from a chemical industry plant. According to the main composition of the real wastewater, synthetic wastewater was made in laboratory. This wastewater contained about 1000 mg/L acetate, 1000 mg/L ethanol and 3000 mg/L sulfate, and had COD/sulfate ratio of approximately 1. Sodium sulfate was used to supply sulfate in the wastewater. $NaHCO_3$ dosage was controlled at 3000 mg/L except at the starting-up HRT of 48 h with dosage of 1500 mg/L. The other constituents in the synthetic wastewater were as follows: NH_4Cl, 850 mg/L; KCl, 750 mg/L; K_2HPO_4, 250 mg/L; KH_2PO_4, 100 mg/L; $MgCl_2{\cdot}6H_2O$, 125 mg/L; $CaCl_2$, 15 mg/L; $FeCl_2{\cdot}4H_2O$, 42 mg/L; $CoCl_2{\cdot}6H_2O$, 4.2 mg/L and $NiCl_2{\cdot}6H_2O$, 4.2 mg/L.

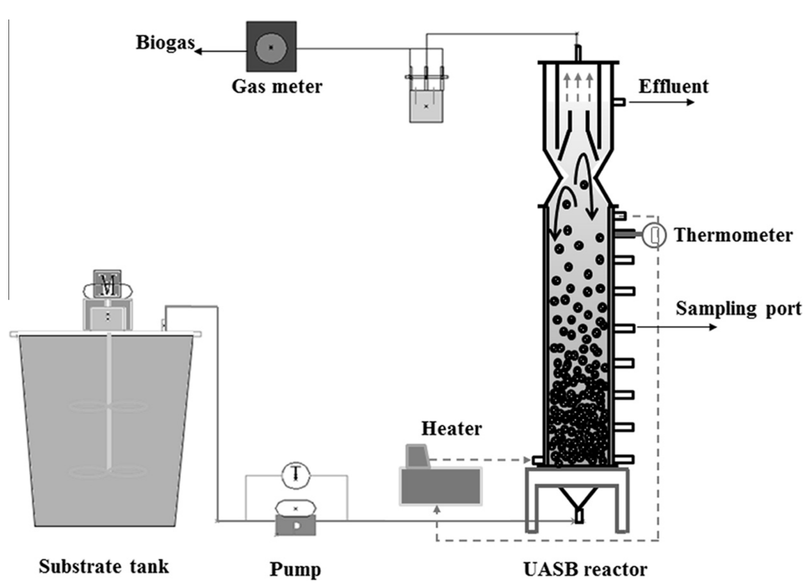

Fig. 1. Schematic diagram of the granular sludge UASB.