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Effect of influent COD/SO_4^{2-} ratios on biodegradation behaviors of starch wastewater in an upflow anaerobic sludge blanket (UASB) reactor

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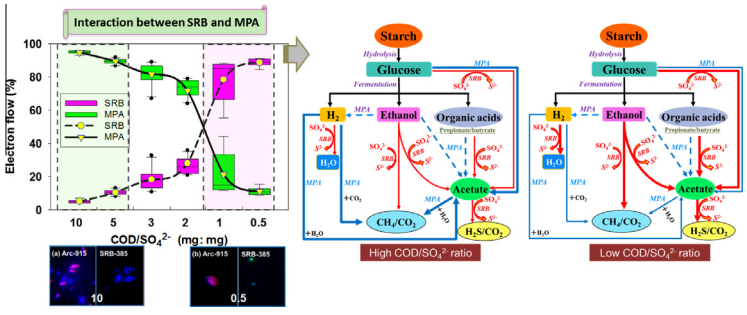
HIGHLIGHTS

- Sulfidogenesis was essential to the UASB operation and process stability.
- Reactor showed the high stability at COD/SO_4^{2-} ratios ⩾2 with efficient removal of COD and sulfate.
- Sulfidogenesis promoted propionate degradation and acetoclastic methanogenesis.
- Excessive sulfidogenesis suppressed methanogenesis, deteriorating bioenergy conversion.

GRAPHICAL ABSTRACT



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ABSTRACT

A lab-scale upflow anaerobic sludge blanket (UASB) has been run for 250 days to investigate the influence of influent COD/SO_4^{2-} ratios on the biodegradation behavior of starch wastewater and process performance. Stepwise decreasing COD/SO_4^{2-} ratio enhanced sulfidogenesis, complicating starch degradation routes and improving process stability. The reactor exhibited satisfactory performance at a wide COD/SO_4^{2-} range ⩾2, attaining stable biogas production of 1.15–1.17 L L^{-1} d^{-1} with efficient simultaneous removal of total COD (73.5–80.3%) and sulfate (82.6 ± 6.4%). Adding sulfate favored sulfidogenesis process and diversified microbial community, invoking hydrolysis–acidification of starch and propionate degradation and subsequent acetoclastic methanogenesis; whereas excessively enhanced sulfidogenesis (COD/SO_4^{2-} ratios <2) would suppress methanogenesis through electrons competition and sulfide inhibition, deteriorating methane conversion. This research in-depth elucidated the role of sulfidogenesis in bioenergy recovery and sulfate removal, advancing the applications of UASB technology in water industry from basic science.

1. Introduction

The world total primary energy demand (TPED) reached 13,579 million tons of oil equivalents (Mtoe) in 2013 (IEA, 2015). It is estimated to be around 15,370 Mtoe by 2030, growing by 75% than in 1990 (8790 Mtoe). Under severe stress of continuing growth in TPED, attempts to seek out renewable energy sources have gained great interest by far (Lu et al., 2015a; Zhen et al., 2015). Methane-rich biofuel production is an excellent fuel and is being widely used world wild. Anaerobic digestion is a superior approach for the treatment of wastewater to produce methane-rich biogas, helping reduce environmental burden and the world's dependency on fossil fuels. So far, a variety of organic wastestreams have been used as substrates to recover the bioenergy. Starch wastewater (SW),

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known as a typical food processing wastewater with high carbohydrate content, is one of the most seriously polluted wastewater (Lu et al., 2015a; Ren et al., 2015); nonetheless it could serve as a low price feedstock for production of potential bioenergy such as methane (Lu et al., 2015b), hydrogen (Xie et al., 2014), or electricity (Lu et al., 2009).

Upflow anaerobic sludge blanket (UASB) is so far one of well-developed processes because of low capital cost, less excess sludge production and especially recovery of methane-rich biogas (Jing et al., 2013; Lu et al., 2015b). Methane production from SW by UASB treatment was reported in a few literature researches. As an example, Annachhatre and Amatya (2000) treated the SW in UASB process and obtained a satisfactory performance, COD removal >95% and biogas productivity of around 8 L L^{-1} d^{-1}. It should be noted that sulfate is commonly presented at significant levels in starch wastewater as high as several 1000 mg L^{-1} (Yoda et al., 1987). Sulfate reduction will occur if sulfate is present although it is a non-toxic and nonvolatile compound (Bertolino et al., 2015). Sulfate reducing bacteria (SRB) utilizing sulfate as the terminal electron acceptor compete with methane producing archaea (MPA) and homoacetogenic bacteria (AB) for carbon sources such as starch or acetate (Hu et al., 2015). The competition of SRB with MPA for electron donors increases with a decrease in the COD/SO_4^{2-} ratio of wastewater due to the kinetic and thermodynamic advantages (Hulshoff Pol et al., 1998). In this regard, besides the influence on the outcome of competition, the influent COD/SO_4^{2-} ratio will also determine the bioenergy recovery efficiency of an UASB process from carbon sources and even impact the overall process performance.

To date, extensive work has been carried out on a wide range of wastestreams with acetate, ethanol (Hu et al., 2015), volatile fatty acids (Oflaherty et al., 1998), sucrose (Lopes et al., 2007; Sabumon, 2008), benzoate (Li et al., 1996), or lactate (Bertolino et al., 2015) as substrates, with the aim of elucidating the effect of COD/SO_4^{2-} ratio on biological treatment of wastewater. Li et al. (2015b) carried out a 196-day UASB experiment to treat chemical synthesis-based pharmaceutical wastewater containing rich organic sulfur compounds and sulfate; at a COD/SO_4^{2-} ratio of 8, a nearly 70% COD reduction occurred with biogas containing 63% methane, but COD/SO_4^{2-} ratio of 1.5 (1212 SO_4^{2-}-S mg L^{-1}) resulted in a inhibition in methanogenesis. Hulshoff Pol et al. (2001) reported that the process failures of anaerobic reactors for methane production took place when the COD/SO_4^{2-} ratio of the wastewater was less than 10. Conversely, in a mesophilic acetate-fed anaerobic reactor, Yang et al. (2015) did not notice significant inhibition of sulfate addition on methane production capacities. Sabumon (2008) even claimed that the enhanced sulfidogenesis at low COD/SO_4^{2-} ratios between 1 and 2 favored process stability and removal of COD and SO_4^{2-}. Despite the great advances achieved before, there is a lack of studies on the effect of COD/SO_4^{2-} ratio on the biological treatment of wastewater with complex organics (Das et al., 2015), such as starch wastewater. In a previous research (Lu et al., 2015b), we demonstrated the benefits of UASB process in treating starch wastewater, which removed 81–99% of total COD_{starch} with methane yield of 0.33 L CH_4 g^{-1} $COD_{removed}$ at HRT 6 h and COD/SO_4^{2-} ratio of 20.0. Nonetheless, the current work still cannot answer whether or not UASB runs smoothly during the long-term operation with a wide range of COD/SO_4^{2-} ratios. More in-depth studies are necessary to understand how the COD/SO_4^{2-} ratio affects the biodegradation routes of starch wastewater as well as subsequent methane production and sulfate reduction. The present study is the continuation of the work.

To accomplish those goals, a lab-scale UASB reactor fed with synthetic starch wastewater has been designed, and continuously run for 250 days under the influent COD/SO_4^{2-} ratios of 10–0.5. The balance of COD and sulfate conversion under different scenarios were calculated to explore the relative portion of electron donor transferred into MPA and SRB. Activity tests were performed to clearly map the biodegradation kinetics of starch. Furthermore, morphological and microbial structures of granular sludge were characterized by scanning electron microscopy (SEM) and fluorescence *in situ* hybridization (FISH). Finally, the energy conversion efficiencies of the reactor under different COD/SO_4^{2-} ratios were calculated, with the purpose of providing more basic data and theoretical guidance for advancing its practical application.

2. Methods

2.1. Reactor and experimental design

An upflow anaerobic sludge blanket (UASB) was packed with a rectangular column with an effective working volume of 6 L (φ 10 cm × 80 cm) and installed a gas–liquid–solid separator (GLS) at the top of reactor. The synthetic starch wastewater was pumped from an influent tank with the volume of 220 L. The detailed schematic diagram of the UASB reactor was shown in our previous research (Lu et al., 2015a). According to the actual compositions of the starch wastewater, the synthetic wastewater was used as influent. The compositions of the synthetic wastewater were as follows (in mg L^{-1}): 1000 COD starch, 2000–2700 $NaHCO_3$, 850 NH_4Cl, 750 KCl, 250 K_2HPO_4, 100 KH_2PO_4, 125 $MgCl_2 \cdot 6H_2O$, 4.2 $NiCl_2 \cdot 6H_2O$, 4.2 $CoCl_2 \cdot 6H_2O$, 15 $CaCl_2 \cdot 2H_2O$ and 42 $FeCl \cdot 4H_2O$. Sulfate was added in the form of Na_2SO_4 to meet the COD/SO_4^{2-} ratio from 10 to 0.5 (phase I–VI).

The reactor was inoculated on September 22, 2014, with 1 L granular sludge taken from a 6-L lab-scale UASB reactor operated at 35 ± 1 °C in our lab, and 3 L anaerobic sludge withdrawn from sludge treatment plant effluent mixture of ethanol and sugar factory waste water in Tokyo, Japan. The sludge added as inoculum occupied 2/3 of the working volume of reactor. The UASB reactor has been continuously run for 250 days, and the operational conditions followed in this study are detailed in Table 1. Organic loading rate (OLR) was gradually increased from 1.0 to 4.0 g COD L^{-1} d^{-1} by reducing HRT from 24 to 6 h (phase I). Once the reactor achieved steady state with more than 80% of COD removed and methane content above 65%, it was operated at a fixed OLR of 4.0 g COD L^{-1} d^{-1} during the subsequent operation (Lu et al., 2015b).

2.2. Activity test

Specific methanogenic activity (SMA) and specific sulfidogenic activity (SSA) of the granular sludge freshly taken at the end of each phase were determined at 35 ± 1 °C in 120 mL serum bottles using starch, glucose, acetate, propionate, butyrate and H_2–CO_2 (v/v: [80:20]) as substrates, respectively. The initial COD concentration was 1000 mg L^{-1}. Na_2SO_4 was added to the serum bottle according to COD/SO_4^{2-} ratio. The experimental procedure was described in detail in our prevenient research (Lu et al., 2015b). Except the biogas production and compositions, the residual sulfate was measured at different intervals, and was converted into equivalent COD based on stoichiometry (i.e. 1 L CH_4 = 2.857 g COD; 1 g SO_4^{2-} = 0.6667 g COD). The SMA and SSA under different COD/SO_4^{2-} ratios were expressed by the curve slope of the methane production and sulfate reduction (Eqs. (1) and (2)).

$$\mathrm{SMA}\left(\frac{\mathrm{gCOD}}{\mathrm{gVSS}\cdot\mathrm{d}}\right) = \mathit{Slope}\left(\frac{\mathrm{Methanogenesis}}{\mathrm{VSS}\cdot\mathrm{d}}\right) \quad (1)$$

$$\mathrm{SSA}\left(\frac{\mathrm{gCOD}}{\mathrm{gVSS}\cdot\mathrm{d}}\right) = \mathit{Slope}\left(\frac{\mathrm{Sulfidogenic}}{\mathrm{VSS}\cdot\mathrm{d}}\right) \quad (2)$$