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Ultrasonic enhancement of waste activated sludge hydrolysis and volatile fatty acids accumulation at pH 10.0

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ABSTRACT

Volatile fatty acids (VFA), the preferred carbon source for biological nutrients removal, can be produced by waste activated sludge (WAS) anaerobic fermentation. However, because the rate of VFA accumulation is limited by that of WAS hydrolysis and VFA is always consumed by methanogens at acidic or neutral pHs, the ultrasonic pretreatment which can accelerate the rate of WAS hydrolysis, and alkaline adjustment which can inhibit the activities of methanogens, were, therefore, used to improve WAS hydrolysis and VFA accumulation in this study. Experiment results showed that the combination of ultrasonic pretreatment and alkaline adjustment caused significant enhancements of WAS hydrolysis and VFA accumulation. The study of ultrasonic energy density effect revealed that energy density influenced not only the total VFA accumulation but also the percentage of individual VFA. The maximal VFA accumulation (3109.8 mg COD/L) occurred at ultrasonic energy density of 1.0 kW/L and fermentation time of 72 h, which was more than two times that without ultrasonic treatment (1275.0 mg COD/L). The analysis of VFA composition showed that the percentage of acetic acid ranked the first (more than 40%) and those of iso-valeric and propionic acids located at the second and third places, respectively. Thus, the suitable ultrasonic conditions combined with alkaline adjustment for VFA accumulation from WAS were ultrasonic energy density of 1.0 kW/L and fermentation time of 72 h. Also, the key enzymes related to VFA formation exhibited the highest activities at ultrasonic energy density of 1.0 kW/L, which resulted in the greatest VFA production during WAS fermentation at pH 10.0.

1. Introduction

Recently, considerable attention has been paid to the enhanced biological phosphorus removal (EBPR) process because no chemical sludge is produced. EBPR is characterized by culturing the polyphosphate accumulating organisms (PAO) under anaerobic–aerobic conditions (Tong and Chen, 2007), and the content and composition of volatile fatty acids (VFA) in wastewater are important for achieving high phosphorous removal performance (Llabres et al., 1999; Chen et al., 2004; Feng et al., 2009). Usually 6.0–9.0 mg of VFA is required for biological removal of 1.0 mg of phosphorus from wastewater (Pitman et al., 1992).

VFA can be produced from waste sludge in wastewater treatment plants (Moser-Engeler et al., 1998; Yuan et al., 2006), by which both sludge reduction and VFA production are accomplished. It is well known that all the three steps, hydrolysis, acidification and methanogenesis are involved in

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a sludge anaerobic digestion process, but the initial hydrolysis of particulate organic matters to soluble substance is identified to be the rate-limiting step, and the VFA produced during sludge anaerobic digestion can be consumed by methanogens (Eastman and Ferguson, 1981). Thus, if the hydrolysis rate was accelerated, and the methanogenesis were, simultaneously, prevented or reduced, VFA accumulation would increase.

In order to accelerate the hydrolysis of organic matters, sludge is often pretreated by various physical and chemical methods, such as thermal treatment (Climent et al., 2007), alkaline treatment (Lin et al., 1997), ozone treatment (Yeom et al., 2002) and ultrasonic treatment (Kazi et al., 2006). Among these methods, ultrasonic treatment is generally regarded as non-hazardous to the environment. Several recent reports have demonstrated the efficiency of ultrasonication as a pretreatment method for disintegrating sludge and thereby accelerating the anaerobic digestion process (Bougrier et al., 2005; Zhang et al., 2007).

It has been documented that acidic pH environments could inhibit the methanogens and produce only organic acids (Elefsiniotis and Oldham, 1996; Yu and Fang, 2002). Until now, some investigators found that strong alkaline pH (such as pH 10.0) could also prevent the methanogens and produce more VFA than acidic pH from sludge (Yuan et al., 2006; Chen et al., 2007).

Although it has been observed that sludge hydrolysis can be enhanced by ultrasonic pretreatment or alkaline adjustment, the ultrasonic pretreatment combined with alkaline adjustment (pH 10.0) to produce VFA from waste activated sludge (WAS) has been seldom investigated. Ultrasonic energy density was a key parameter observed in our research, which influenced WAS hydrolysis and VFA accumulation. The purpose of this study was, therefore, to investigate how ultrasonic pretreatment influenced WAS hydrolysis and VFA accumulation at different energy densities and pH 10.0. The composition of VFA was examined, and the mechanisms for enhanced VFA production ultrasonically were discussed. Also, the releases of ammonium and phosphorus from WAS were studied.

2. Material and methods

2.1. Source of WAS

The WAS used in this study was obtained form the secondary sedimentation tank of a municipal wastewater treatment plant (WWTP) in Shanghai, China. The sludge was concentrated by settling at 4 °C for 24 h and its main characteristics are shown in Table 1. As shown in Table 1, protein and carbohydrate are the two predominant kinds of organic compounds in WAS.

2.2. Batch fermentation experiments

The ultrasonic pretreatment of WAS was performed with an ultrasonicator (US Sonics, VCX 105) at a frequency of 20 kHz and time of 10 min. The ultrasonic-pretreated WAS was stored at 4 °C for the fermentation tests. Effects of ultrasonic energy density on WAS hydrolysis and VFA accumulation were conducted in a series of fermentation reactors, which were made of plexiglass and each had a working volume of 1.0 L with internal diameter of 100 mm and height of 150 mm. All reactors were stirred at a speed of 80 rpm (revolutions per minute) for mixing the contents.

Table 1 – Characteristics of WAS.[a]

Parameter	Mean
pH	6.5
TSS (total suspended solids)	10,119
VSS (volatile suspended solids)	6982
TCOD (total chemical oxygen demand)	10,004
Total carbohydrate (as COD)	1026
Soluble carbohydrate (as COD)	23
Total protein (as COD)	6159
Soluble protein (as COD)	44
Ammonia nitrogen ($NH_4^+ - N$)	10.2
Soluble phosphorus ($PO_4^{3-} - P$)	25.4

a All values are expressed in mg/L except pH.

During the fermentation tests of ultrasonic-pretreated WAS, the energy density was controlled at 0.25, 0.5, 1.0, 2.0 and 4.0 kW/L in reactors 1–5, whose pHs were adjusted to 10.0 by adding 2 M sodium hydroxide (NaOH) or 2 M hydrochloric acid (HCl). Reactor six and seven were set as blank test one (ultrasonic pretreatment (1.0 kW/L) and no pH adjustment) and blank test two (no ultrasonic pretreatment and pH 10.0), respectively. The temperatures in all fermentation reactors were controlled at 20 ± 1 °C. After the ultrasonic-pretreated WAS was added into the reactors, the fermentation time was recorded.

2.3. Analytical methods

The sludge samples from the reactors were centrifuged at 10000 rpm for 10 min and then immediately filtered through a Whatmann GF/C glass microfiber filter (1.2 μm pore size). The filtrate was immediately analyzed for VFA, carbohydrate and protein. The analyses of total suspended solids (TSS) and volatile suspended solids (VSS) were conducted in accordance with Standard Methods (American Public Health Association, 1998). Carbohydrate was measured by the phenol–sulfuric method with glucose as the standard (Herbert et al., 1971). Soluble protein was determined by the Lowry–Folin method with BSA as the standard (Lowry et al., 1951). The total protein content of sludge was estimated from the corresponding TKN concentration by subtracting the inorganic nitrogen concentration and dividing the difference by 0.16, then multiplying the result by 1.5 (Miron et al., 2000).

To analyze VFA the filtrate was collected in a 1.5 mL gas chromatography (GC) vial and 3% H_3PO_4 was added to adjust the pH to approximately 4.0. An Agilent 6890 GC with flame ionization detector and DBWAXTRE column (30 m × 0.32 mm × 0.25 mm) was utilized to analyze the concentration and composition of VFA. Nitrogen was the carrier gas and the flux was 50 mL/min. The injection port and the detector were maintained at 200 and 220 °C, respectively. The oven of GC was programmed to begin at 110 °C and to remain there for 2 min, then to increase at a rate of 10 °C/min to 200 °C, and to hold at 200 °C for an additional 2 min. The sample injection volume was 1.0 μL.