



Synergistic effect of free nitrite acid integrated with biosurfactant alkyl polyglucose on sludge anaerobic fermentation



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ABSTRACT

This study reports a new strategy, i.e. combination of free nitrite acid (FNA) and biosurfactant Alkyl polyglucose (APG), for the production of short chain fatty acids (SCFA) from sludge anaerobic fermentation. The results showed that when FNA concentration was 1.54 mg/L, the maximum yield of SCFA was 354.6 mg/g, which was significantly higher than that of FNA or APG alone. The combination of FNA and APG also shortened the optimal fermentation time to 5 d. Mechanism studies showed that FNA combined with APG can promote the sludge disintegration. By detecting the degradation of the simulated compounds in the synthetic water, it is found that the FNA combined with APG can synergistically promote sludge hydrolysis and acidification but seriously inhibit the methanogenesis process. The enzyme activity analysis was also consistent with the above experimental results. The combination of FNA and APG in this study provides a promising strategy for enhancing sludge anaerobic fermentation.

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1. Introduction

The waste activated sludge (WAS) is produced in large quantities as a by-product of the activated sludge process in wastewater treatment plants (WWTPs) (Zhao et al., 2018). It is reported that the annual amount of dry sludge production in China is as high as 11.2 million tons (Feng et al., 2015). WAS contains a large number of toxic pollutants, pathogens and parasites, causing potential threats to the environment and human health if the WAS is not treated properly (Zhao et al., 2015a,b). In addition, the cost of WAS management is high, accounting for up to approximately 60% of the operating cost in the WWTPs (Kim et al., 2016). Anaerobic digestion of WAS is considered to be the most effective sludge treatment strategy, where pathogens and bacteria can be killed, the sludge volume is reduced, and energy sources such as methane and hydrogen can be generated, simultaneously (Feng et al., 2009; Chen et al., 2013; Zhao et al., 2016a,b, 2014; Hassan et al., 2017; Li et al., 2018). Recently, the production of short-chain volatile fatty acids (SCFA) from WAS anaerobic fermentation has attracted the scholars' attention because the SCFA produced can not only be utilized as a preferred carbon source to enhance sewage treatment but also can be used as raw materials for biodegradable plastic synthesis (Wang et al., 2016; Zhao et al., 2015c, 2017a,b).

Anaerobic fermentation of WAS consists of four consecutive processes, namely disintegration, hydrolysis, acidification and methanogenesis (Zhao et al., 2016c, 2017b). SCFA is generated in the acidification stage and rapidly consumed by methanogens in the methanogenesis phase (Zhao et al., 2016c). Therefore, the common practice to improve the accumulation of SCFA is to accelerate the hydrolysis step and inhibit the activities of methanogen (Zhang et al., 2015a; Zhou et al., 2015). For example, alkaline fermentation (eg, pH 10) accelerates the destruction of sludge flocs and severely compromises the activity of methanogens resulting in SCFA accumulation (Zhao et al., 2015a; Ma et al., 2016). In addition, the optimal fermentation time was also significantly reduced compared to the blank (Torres and Lloréns, 2008). Yan et al. (2010) investigated the effects of ultrasonic pretreatment on WAS alkaline fermentation, and the results showed that ultrasonic pretreatment can significantly promote the bioproduction of SCFA from WAS alkaline fermentation, and the optimal ultrasonic energy density was 1.0 Kw/L (Yan et al., 2010). Enzyme pretreatment to promote sludge hydrolysis and SCFA accumulation has also been reported (Xin et al., 2018). Although these strategies have been very effective in enhancing sludge hydrolysis and inhibiting methanogenesis, resulting in the accumulation of SCFA, they are energy-intensive, heavily depleted on chemical reagents or environment secondary pollution, making it difficult to implement in some small or technical backwardness WWTPs. Therefore, some energy-saving and environment-friendly sludge pre-treatment methods need to be developed and applied urgently.

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Biosurfactant alkyl polyglucose (APG) is a comprehensive new type of non-ion surfactants, with the characteristics of high surface activity, non-toxic, rapid biodegradable and easy to use. In addition, compared with other biological surfactants, APG was relatively low cost and efficient. APG has been applied to improve membrane sludge and WAS anaerobic fermentation, and it was found that APG promoted disintegration, hydrolysis and acidification, however, inhibited the methanogenic process, thereby accumulating the production of SCFA (Xu et al., 2016; Zhao et al., 2015c). In addition, the price of APG is relatively reasonable. Therefore, APG-based technology is potential and promising to enhance anaerobic fermentation of sludge. However, the efficiency of APG enhanced SCFA production is not satisfactory. Furthermore, microwave pretreatment combined with APG have a synergistic effect on sludge anaerobic fermentation, and the main functional microorganism was *Lactobacillus* (Xiao et al., 2017). Although microwave pretreatment combined with APG can further improve the degree of sludge hydrolysis and SCFA yield, microwave pretreatment has energy consumption characteristics, which is the main drawback of this combined technology. Whether APG in combination with other low-cost technologies will have a synergistic effect on sludge anaerobic fermentation remains unknown.

Nitrite can be obtained as the by-product of sewage treatment fermentation liquid, and the concentration of nitrite can be as high as 1500 mg/L (Wang et al., 2013), so nitrite can be introduced into the sludge fermentation system in situ. Free nitrous acid (FNA), protonated form of nitrite, has been proved to be an effective biocide agent for microorganisms in biofilms and WAS systems (Zahedi et al., 2017; Pijuan et al., 2012). FNA can destroy the cell wall and/or membrane through a series of reactions with lipids, proteins and carbohydrates. Recently, Wang et al. (2013) demonstrated that the hydrolysis rate and biochemical methane potential of the WAS with 2.13 mg/L FNA pretreatment for 24 h were significantly increased, which promoted the anaerobic digestion of sludge (Wang et al., 2013). Our previous results showed that FNA could accelerate the lysis of extracellular polymers and cell envelope to improve the efficiency of alkaline fermentation (Zhao et al., 2015a). FNA combined with other processing technologies such as heat treatment, hydrogen peroxide, and chemical surfactants can also promote sludge hydrolysis by destroying macromolecular organic compounds, thereby promoting sludge anaerobic digestion (Zhang et al., 2015b). However, there is still some potential disadvantage of input of certain energy or secondary pollution in the above technologies. Considering the high efficiency and non-toxicity of biosurfactant APG, FNA combined with APG may have a synergistic effect on sludge anaerobic fermentation, which is beneficial to resource recovery. To date, however, this hypothesis has not been experimentally verified and the corresponding mechanism remains unclear.

Therefore, this paper investigates the impact of FNA combined with APG on sludge anaerobic fermentation. First, the yields of SCFA at different concentrations of FNA in combination with APG were compared and the optimal FNA concentration was obtained. Second, the mechanisms of synergistic effect of FNA integrated with APG on WAS anaerobic fermentation were explored from sludge disintegration, hydrolysis, acidification and methanogenesis. Finally, the potential significance of FNA combined with APG for sludge anaerobic fermentation was completely elaborated.

2. Materials and methods

2.1. Sludge source

The sludge used in this study was taken from the secondary sedimentation tank of a WWTP in Changsha, China. The sludge

was first filtered to remove indigestible inorganic matter (such as stone, plastic and wooden sticks) and the supernatant was then removed by settlement for 24 h in the laboratory. Finally, the concentrated sludge was stored in a 4 °C refrigerator for experimental utilization. The main characteristics of the concentrated WAS are as follows: pH 6.9, total suspended solids (TSS) 13250 mg/L, volatile suspended solids (VSS) 8590 mg/L, total chemical oxygen demand (TCOD) 15320 mg/L, soluble COD 312 mg/L, total protein, 8540 mg/L, total polysaccharide 1203 mg/L.

2.2. Effect of FNA dosage on APG induced sludge anaerobic fermentation

The concentration of FNA directly affects the sludge disintegration and microbial activities, therefore, it is necessary to explore the effect of FNA concentration on APG-induced sludge anaerobic fermentation. This study was conducted in six identical anaerobic reactors (R1-6) with working volume of 2.0 L each. First, 1.6 L of WAS was pumped into each reactor and a certain amount of APG was added R1-5 to control its content of 0.2 g/g according to this literature (Zhao et al., 2015c). Nitrite can be obtained from the sludge digested liquid in situ. The concentration of nitrite is about 1000 mg/L, and the maximum can be as high as 1500 mg/L (Wang et al., 2013). Then, different concentrations of sodium nitrite were added into R1-5 and control their concentrations were 0, 200, 300, 600, and 900 mg/L, respectively. The concentration of nitrite in R7 (defined as FNA reactor) was 600 mg/L, but R7 did not contain APG. Biochemical reaction temperatures can generally be divided into low (~15 °C), medium (20–30 °C) and high (> 35 °C) temperature reactions. High temperature reactions require inputting a large amount of energy, which is not economically viable, while low temperature reactions reduce microbial metabolism. Therefore, medium temperature was selected in this study. Previous studies have shown that there was no significant difference in the reaction within the medium temperature range (Zhao et al., 2015b; Sun et al., 2017; Song et al., 2016). Therefore, this study further selected 20 °C. The pH in each reactor was maintained at pH 6 for 2 d and then adjusted to an initial pH7 by adding 2.0 M sodium hydroxide on the third day, and the pH in each reactor was not constantly controlled during the subsequent fermentation process. WAS contains a large number of hydrolyzed and acidified bacteria. WAS can be used as both fermentation substrate and inoculum. Therefore, no inoculum was added in this study. The pH, temperature and nitrite concentrations used in this study resulted in the initial FNA concentrations of 0, 0.51, 0.77, 1.54 and 2.31 mg/L, respectively, according to the formula $FNA = S_{NO_2-N} / (K_a \times 10^{pH})$, where the value of K_a is determined by the formula $K_a = e^{(-2300/(T+273))}$ for a given temperature (Anthonisen et al., 1976).

2.3. Effect of FNA integrated with APG on sludge disintegration

In this batch experiment, six identical anaerobic reactors were set up to compare and evaluate the effect of FNA integrated with APG on sludge disintegration. Heat pretreatment and BESA were reported to be effective in inhibiting the activities of methanogens (Feng et al., 2014), thus the WAS used in this study was first subjected to heat and BESA treatment. 9.6 L of WAS was pretreated with 102 °C for 30 min. After the mixed WAS was cooled, a 50 mM BESA was added to the WAS and thoroughly mixed to inhibit methanogens activity, and then the above WAS was evenly distributed into the six reactors. The applied concentrations of FNA and APG are the same as described in Section 2.2. The entire experiment lasted 5 d, and the changes in organics content and extracellular polymers (EPS) in the fermentation liquid were monitored daily.

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