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Short Communication

Enhancing sludge biodegradability and volatile fatty acid production by tetrakis hydroxymethyl phosphonium sulfate pretreatment

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HIGHLIGHTS

- THPS was applied to inactivate and disrupt sludge for the first time.
- THPS enhanced organics release and improved sludge biodegradability.
- THPS markedly increased VFA production and shortened fermentation time.
- THPS benefited to high molecular weight VFA generation.

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ABSTRACT

A new pretreatment method based on tetrakis hydroxymethyl phosphonium sulfate (THPS) biocide was tried to enhance sludge disintegration, and improved sludge biodegradability and subsequent volatile fatty acid (VFA) production. Sludge activity decreased to less than 10% after 2 days pretreatment using 20 mg/g-TSS THPS, which also obviously destroyed EPS and cell membrane, and dissolved more biodegradable substances (48.8%) than raw sludge (19.7%). Moreover, 20 mg/g-TSS THPS pretreatment shortened fermentation time to 4 days and improved VFA production to 2778 mg COD/L (4.35 times than that in control). Therein, the sum of n-butyric, n-valeric and iso-valeric acids unexpectedly accounted for 60.5% of total VFA (only 20.1% of that in control). The more high molecular weight VFAs (C4-C5) than low molecular VFAs (C2-C3) resulted from THPS pretreatment benefited to subsequent medium-chain volatile acids (C6-C12) generation to realize the separation and recovery of organic carbon more efficiently.

1. Introduction

Increasing attentions for the depletion of limited and non-renewable fossil fuels in recent years along with the rising global demand for continual manufacture bring about unprecedented concern for biofuels production. Cost-effective anaerobic fermentation for volatile fatty acid (VFA) production from unmanageable excess sludge (ES) is potential to simultaneously realize environmental and economic sustainable development. As a green platform chemical, VFA has a higher additional value than methane (Tamis et al., 2015) and a superiority of versatility in subsequent conversion (Reyhanitash et al., 2015). For instance, VFA can be used for enhancing nitrogen/phosphorus removal from wastewater (Feng et al., 2009), recovering medium chain fatty acid (MCFA) (Steinbusch et al., 2011), synthesizing polyhydroxyalkanoate (Chen et al., 2013a) and generating electricity (Chen et al., 2013b), etc.

However, the inferior bio-availability of intracellular organics in sludge limits VFA yield and raises production difficulty. Most of sludge nutrients including protein and carbohydrate are embedded in cell wall and immobilized in floc structure (Xie et al., 2016). Sludge flocs and cells are linked together by tridimensional and gelatinous extracellular polymeric substances (EPS), which isolate cells and extracellular enzymes and prevent intracellular constituents from releasing into aqueous phase (Yuan et al., 2014). Besides, plenty of crosslinked polymers in cell envelope also prevent bioconversion process of microorganism on organics (Xie et al., 2016). Hence, efficient pretreatment is required to destroy EPS and cell wall and improve the biodegradability of sludge for subsequent bio-utilization. Previous sludge pretreatment methods like ultrasonic, microwave, pyrolysis, alkaline and acid gained obvious promotion effect, but frequent power input, massive chemical requirement, potential ecological pollution and high pro-

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cessing expense impeded its practical application (Wu et al., 2017). Hence, an alternative cost-effective and eco-friendly method is still urgently needed.

Tetrakis hydroxymethyl phosphonium sulfate (THPS), the owner of 1997 "Designing Greener Chemicals Award" from the US Environmental Protection Agency, is a fully water-soluble quaternary phosphonium salt and is originally used as a green and cheap bactericide in industrial cooling water systems (Guo et al., 2014). THPS is readily biodegradable and cannot accumulate in environment for its easy and rapid oxidation to trishydroxymethylphosphine oxide (THPO), which can be further mineralized to carbon dioxide, water and phosphate (Paulus, 1993).

THPS presented a strong bactericidal ability at the concentration of above 15 mg/L (Zhao et al., 2009) and targeted against wide range of bacteria (Okoro, 2015). So far, most reports on the biocidal efficacy of THPS focused on sulfate-reducing bacteria and oil pipeline liquid biofilms, which were drastically inhibited by penetrating bacterial biofilms (Okoro, 2015; Xu et al., 2012). Recently, Li et al. (2016) reported THPS as a metabolic uncoupler had the ability to reduce sludge production and growth yield (Li et al., 2016). In addition, THPS was also a surfactant, which could enhance sludge hydrolysis and acidification during sludge anaerobic fermentation just as other surfactants such as rhamnolipid, surfactin, saponin and sodium dodecylbenzenesulfonate (Huang et al., 2015; Zhao et al., 2016). To date, however, very little research was documented on the biocidal effect of THPS on sludge that was primarily formed by microorganisms (Xie et al., 2016). We hypothesized the biocidal ability of THPS could inactivate sludge, lyse cells, improve sludge biodegradability and enhance subsequent bio-utilization efficiency.

Consequently, the main objectives of this study were to (1) confirm the feasibility of THPS on devitalizing sludge and disintegrating EPS and cell wall; (2) survey the availability of THPS on enhancing extracellular/intracellular organics dissolution and improving sludge biodegradability; (3) investigate the influences of THPS pretreatment on VFA production and component.

2. Materials and methods

2.1. ES and THPS

The sources and characteristics of ES were shown in Supplementary Information (SI). 10 g/L THPS stock solution was prepared before use with THPS (75% solution) that was supplied by YuanYe biological company (Shanghai, China).

2.2. THPS pretreatment

Seven identical glass bottles were used for THPS pretreatment to assess its effects on sludge activity and EPS and cell envelope disruption. Each bottle was fed with 500 mL sludge, and then different volumes of the THPS stock solution were added to reach THPS dosages of 0, 3, 6, 10, 15, 20 and 30 mg/g-TSS, respectively. Finally, all bottles were stirred in an air bath shaker with rotating speed of 150 rpm and temperature of 30 °C.

The specific oxygen utilization rate (SOUR) of each reactor was monitored to evaluate the effect of THPS on sludge activity after 2 days pretreatment. Quantitative samples were regularly taken to measure released SCOD, protein and carbohydrate concentrations in dissolved organic matter (DOM). The residual sludge pellet was subsequently re-suspended in distilled water and extracted EPS with a heat extraction method (Li and Yang, 2007) to measure organics variations in loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS). Furthermore, to investigate the effects of THPS pretreatment on cell envelop disruption and eliminate the influence of EPS on cell envelope, the raw sludge that was removed EPS was utilized to implement THPS pretreatment test just like the methods described above.

2.3. Effect of THPS pretreatment on sludge biodegradability and VFA production

Two experiments including analyzing the DOM distribution of THPS pretreated sludge during anaerobic fermentation process by EEM and FRI and measuring organics consumption efficiency by aerobic digestion were conducted to evaluate the variation of sludge biodegradability, and the detailed steps were described in SI.

VFA production was carried out with seven identical anaerobic reactors that were severally added with 350 mL pretreated sludge with different THPS dosages mentioned in 2.2. Then, 30 mL raw sludge was seeded into each reactor as the inoculum, and the pH was adjusted to 6. Finally, all the reactors were flushed with nitrogen gas for 10 min to remove oxygen, and stirred in an air bath shaker (150 rpm, 30 °C) for 7 days. All the experiments were performed in parallel triplicates.

2.4. Analytical methods

The determination methods of all the parameters and data were shown in SI.

3. Results and discussion

3.1. Effect of THPS on sludge activity and disintegration

The deactivation effect of THPS on sludge was evaluated by the SOUR variation (Fig. S1), which was well described by an exponential model, and the decreasing rate of microbial activity was 1/7.83. Sludge activity markedly declined with rising THPS dosages according to SOUR value, which decreased by 91.7% after 20 mg/g-TSS THPS pretreatment compared with control, and the sludge almost entirely lost activity at a higher THPS dosage of 30 mg/g-TSS. The inactivation ability mainly stems from THP, which is the dissociation product of THPS and can deactivate the proteins in cell walls of microorganisms (Paulus, 1993).

EPS and cell envelop play a major role in protecting sludge cell from external damage, thus their disruptions are closely related with cell disintegration (Zhao et al., 2015). The released soluble organics at the initial 14 h THPS pretreatment could symbolize EPS disruption, which was expressed in terms of soluble COD, protein and carbohydrate variations in DOM, LB-EPS and TB-EPS (Fig. 1). Clearly, all the THPS dosages contributed to organics dissolution and higher THPS level showed better promoting effect on EPS disruption. At 20 mg/g-TSS THPS, SCOD, protein and carbohydrate concentrations in DOM increased by 2.89, 2.91 and 2.60 times compared with control, respectively, while higher THPS dosages showed insignificant improvement ($P > 0.05$) on organics dissolution. In LB-EPS, organics dissolution also increased with THPS dosages. Unlike LB-EPS, organics in TB-EPS decreased apparently with THPS addition, and the SCOD, protein and carbohydrate concentrations at 20 mg/g-TSS were only 39%, 43% and 40% of the control, respectively. It was implied that 20 mg/g-TSS THPS dosage was adequate to destroy EPS, subsequently releasing inner nutrients from sludge floc into the aqueous phase. Furthermore, sludge without EPS was used to reveal the effect of THPS pretreatment on cell membrane. From Fig. 2, THPS pretreatment assuredly helped to disrupt cell membrane, therein, 20 mg/g-TSS gained 137%, 156% and 269% higher protein, carbohydrate and DNA dissolutions than those in control, respectively, and showed insignificant discrep-