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Enhanced short-chain fatty acids production from waste activated sludge by combining calcium peroxide with free ammonia pretreatment

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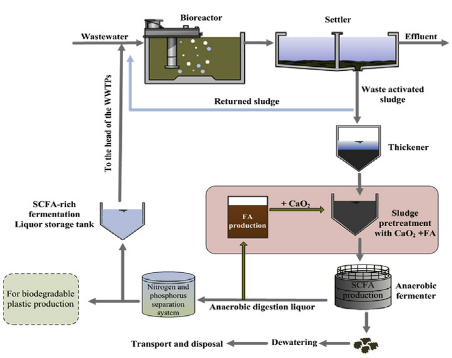
GRAPHICAL ABSTRACT



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ABSTRACT

This study reported a new low-cost and high-efficient combined method of CaO_2 + free ammonia (FA) pretreatment for sludge anaerobic fermentation. Experimental results showed that the optimal short-chain fatty acids (SCFA) yield of 338.6 mg COD/g VSS was achieved when waste activated sludge (WAS) was pretreated with 0.05 g/g VSS of CaO_2 + 180 mg/L of FA for 3 d, which was 2.5-fold of that from CaO_2 pretreatment and 1.5-fold of that from FA pretreatment. The mechanism investigations exhibited that the CaO_2 + FA could provided more biodegradable substrates, this combination accelerated the disintegration of sludge cells, which thereby providing more organics for subsequent SCFA production. It was also found that the combination of CaO_2 and FA inhibited the specific activities of hydrolytic microbes, SCFA producers, and methanogens to some extents, but its inhibition to methanogens was much severer than that to the other two types of microbes.

1. Introduction

With the wide use of activated sludge process in the treatment of municipal wastewater, large quantities of waste activated sludge (WAS), are inevitably produced in wastewater treatment plants (WWTPs) (Leng et al., 2018; Li et al., 2016b; Wang et al., 2017d; Zhao et al., 2015). Treatment and disposal of WAS is now becoming one of the major challenges faced by WWTPs, with its cost accounting for up to

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60% of the total operation costs of a WWTP (Stasinakis, 2012; Wang et al., 2017b; Xu et al., 2017). Meanwhile, WAS also contains high concentrations of organics (e.g. proteins and carbohydrates), which could be further re-captured for energy recovery (e.g. short-chain fatty acid and methane production) (Dai et al., 2017; Hu et al., 2018; Zhao et al., 2017b). Hence, reutilization of WAS to produce short-chain fatty acid (SCFA) via anaerobic fermentation has recently attracted increasing interests (Xu et al., 2018; Zhao et al., 2015), as the produced SCFA is a value-added product that could be employed as either a raw substrate for biodegradable plastic production or a preferred carbon source for biological nutrient removal microbes (Chen et al., 2017; Jiang et al., 2009; Wang et al., 2017a; Yi et al., 2017). However, operation of the WAS anaerobic fermenters is often upset even at bench-scale. For example, SCFA production via anaerobic fermentation is usually limited by the slow WAS disintegration rate and rapid consumption by methanogens (Chen et al., 2013; Yuan et al., 2006). As the byproduct of wastewater treatment, WAS not only collects various biodegradable-organics but also concentrates substantial non-degradable organic pollutants, such as endocrine disrupting compounds and pharmaceuticals and personal care products(Yang et al., 2018). These emergencing pollutants are generally toxic and are not degraded in the conventional WAS fermentation or digestion process (Muller et al., 2010; Wang et al., 2017e), which thereby affect anaerobic fermentation and pose potential threats to ecological environment. Therefore, pertinent pretreatment on WAS is usually implemented prior to anaerobic fermentation (Li et al., 2016a, 2015; Zhao et al., 2017a).

Calcium peroxide (CaO_2), which is a solid peroxide and has a high-energy peroxide covalent bond, could slowly decompose to form O_2, H_2O_2, and $Ca(OH)_2$ at a “controlled” rate in hydrous media (Qian et al., 2013). Due to its characteristic, CaO_2 has been extensively utilized in several fields such as in-situ bioremediation of contaminated soil and ground water (Liu et al., 2006; Xu et al., 2011). Recently, some scientists or engineers exploited another novel direction, i.e., being an additive to pretreat WAS for the enhancements of SCFA production, dewaterability, and endocrine disrupting compound degradation (Chen et al., 2016; Li et al., 2015; Zhang et al., 2015). For instance, Li et al. (2015) demonstrated that CaO_2 significantly accelerated the WAS disintegration but inhibited the activity of methanogens, which therefore benefited SCFA production. They found that the maximum SCFA production (284 mg COD/g VSS) occurred at a CaO_2 dose of 0.2 g/g VSS and fermentation time of 7 d, which was 3.9-fold higher than that without CaO_2 addition (Li et al., 2015). The findings obtained by Li et al. (2015) expanded the application field of CaO_2 and provided a new pretreatment method for SCFA production from WAS. Despite this significant contribution, the dosages of CaO_2 reported are at high levels (e.g., 0.2 g/g VSS), and such levels of CaO_2 dosages inevitably require high operational cost. This diminishes its values to some extents and hinders the further application in real-world situations. CaO_2 could not completely inhibited methanogenesis (Li et al., 2015), which result in low levels of SCFA accumulation. Thus, any improvement that could lower the addition of CaO_2 in an economic and sustainable way should have economic and ecological benefits.

Free ammonia (FA, i.e., NH_3), the non-ionized form of ammonium, was demonstrated to exert a strong biocidal impact on broad microorganisms involved in wastewater and WAS treatment at parts per million levels, because hydrophobic FA could result in proton imbalance and/or potassium deficiency by diffusing passively through the membrane and into the cell (Belmonte et al., 2011; Chen et al., 2008). Previous investigations found that the presence of FA in WAS treatment process inhibited severely methane production (Northup and Cassidy, 2008), with the activity of methanogenic being inhibited by 80% at an FA concentration of 40 NH_3-N/L (Belmonte et al., 2011; Dai et al., 2017). Recent publications further suggested that FA benefited the process of WAS disintegration (Wang et al., 2017c; Wei et al., 2017). Several methods have been applied to enhance SCFA production from WAS (See in E-supplementary data). Although these technologies showed some positive effects, high operational cost, low SCFA accumulation and high energy input hindered its scale-up application. Based on the information documented in the literature, it is hypothesized that the FA-supported approach, i.e., combining CaO_2 with FA pretreatment might be a solution to lower the dosage of CaO_2 and even enhance SCFA production. If this hypothesis is confirmed, this combination pretreatment method will have significant benefits in both economic and practical aspects, since FA is a renewable and cost-effective substance that can be produced directly from anaerobic fermenter effluent through recycling a part of fermentation liquid into the pretreatment unit. However, to date, it is unknown whether the combination of CaO_2 with FA causes a synergistic effect on WAS disintegration. In addition, the potential effect of this combined pretreatment on other biological processes involved in anaerobic fermentation such as hydrolysis, acidogenesis, and methanogenesis also remains unknown.

This work therefore aims to assess the feasibility of whether the combination of CaO_2 and FA pretreatment promotes the production of SCFA from WAS and to understand how this combination pretreatment works or not. To obtain comprehensive information, the effect of pretreatment of WAS with different CaO_2 (0.02, 0.05, or 0.1 g/g VSS) + FA (60, 120, 180, or 240 mg/L) on SCFA production was first assessed. Then, the details of how this combination pretreatment enhances SCFA production were explored by analyzing its impact on the processes of sludge disintegration, hydrolysis, acidogenesis and methanogenesis. The findings acquired in this study advanced the application of CaO_2-based pretreatment in real-world situations and may help to develop a promising approach for both emergencing pollutant removal and energy recovery in the WAS treatment process.

2. Materials and methods

2.1. Waste activated sludge characterization

The WAS used in this study was withdrawn from the secondary sedimentation tank of a municipal WWTP located in Changsha, China. The collected WAS was first filtered with a 1 mm × 1 mm screen and then concentrated for 24 h at 4 °C before use. The main characteristics of the concentrated sludge are as follows: pH (6.8 ± 0.1), total suspended soils, TSS (15860 ± 260 mg/L), volatile suspended soils, VSS (13020 ± 90 mg/L), total COD (12380 ± 150 mg/L), soluble COD (203 ± 120 mg/L), total protein (7810 ± 110 mg COD/L), total carbohydrate (1430 ± 70 mg COD/L), SCFA (16.6 ± 0.8 mg/L), NH_4^+-N (28.2 ± 1.2 mg/L), PO_4^{3-}-P (18.6 ± 0.8 mg/L).

2.2. Pretreatment of sludge and batch anaerobic digestion tests

This batch test was performed in twenty-two replicate fermenters with a working volume of 1 L each. Each of the fermenters was first fed with 500 mL of the concentrated WAS. Then, different amounts of CaO_2 and different volumes of NH_4Cl stock solution (4.0 M) were added into the fermenters at the beginning of the test, respectively, resulting in the initial CaO_2 dosage of 0, 0.02, 0.05, or 0.1 mg/g VSS and initial NH_4^+-N concentration of 28.2, 136.4, 272.8, 409.2, or 545.6 mg/L. It should be emphasized that no extra NH_4^+-N was added into fermenters 1–6, and 28.2 mg/L NH_4^+-N was the background ammonium concentration. Among these fermenters, fermenter 1 was set as the blank without additions of any chemical. Fermenter 2 and fermenter 3 were respectively used to assess the contributions of alkaline (pH 9) and alkaline (pH 9) + CaO_2 (0.05 mg/g VSS) pretreatments to the production of SCFA, while fermenters 4–6 were employed to evaluate the impact of different dosages of CaO_2 alone on SCFA production. The remainder fermenters were utilized to investigate the effect of pretreatment of WAS with different CaO_2 + FA on SCFA production. The experimental conditions for these fermenters are detailed in Table 1.

Except fermenter 1 (i.e., the blank) and fermenters 4–6, the tested WAS in all other fermenters was pretreated under alkaline condition