



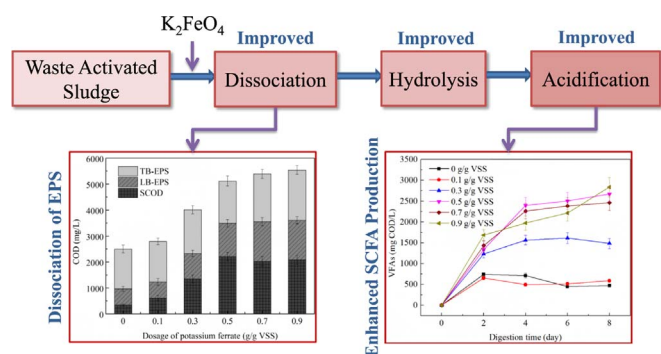
Enhanced bioproduction of short-chain fatty acids from waste activated sludge by potassium ferrate pretreatment



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GRAPHICAL ABSTRACT



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ABSTRACT

Recently, bioproduction of short-chain fatty acids (SCFA) from waste activated sludge (WAS) has attracted much attention. Many pretreatment methods were investigated to improve the hydrolysis efficiency of WAS. However, studies on sludge pretreatment employing ferrate (VI) remain limited. Therefore, this literature explored how the potassium ferrate affects the SCFA production as well as the underlying correlation between the microbial community and the system performance. It was found that the ferrate pretreatment promoted the SCFA production significantly after 8 days' digestion from 475 mg COD/L of the control to 2835 mg COD/L at a dosage of 0.9 g/g. The analysis of extracellular polymeric substance (EPS) showed that the extracted EPS had a positive linear relationship with the final SCFA production, which indicated that the extracted EPS could be adopted as an excellent indicator to reveal the pretreatment effect of this method. The concentrations of protein and carbohydrate both showed uptrends with the increasing dosage of potassium ferrate, whereas it imposed a negative impact on the phosphate concentration, which could be explained by precipitation of Fe ion and phosphate. Terminal restriction fragment length polymorphism (T-RFLP) analysis showed that the biodiversity and population distribution evenness were reduced markedly and it further indicated that ferrate pretreatment enhanced the community function by giving rise to acid-producing bacteria, which was in accord with the observed SCFA yield.

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1. Introduction

A considerable amount of waste activated sludge (WAS) was produced as a byproduct of wastewater treatment plants with over 11.2 million tons of dry sludge generated annually in China, and 10 million tons in EU countries [1–3]. It caused many environmental risks, including the pathogens and parasites existed in WAS for threatening the public health because of possible contact with vectors infectious to humans [4,5], and other toxic pollutants with the potential detriments on contaminating waters and soils such as heavy metals (chromium, lead, mercury, cadmium, etc.) and recalcitrant pollutants (endocrine disruptors, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, etc.) [5,6]. One of the most widely applied solutions to the WAS management is anaerobic digestion, where organic matters in WAS are converted to methane [7]. However, methane is a low-value product and it would deteriorate the economic attractiveness when the government subsidies and policies are absent [8,9]. The short-chain fatty acids (SCFA), which is another choice from anaerobic digestion, is a preferred carbon source for enhanced biological nutrition removal and bioplastic synthesis [10]. Moreover, the SCFA production is much faster than methane production owing to a shorter generation time of acid-producing bacteria compared with methanogens. Therefore, intensive studies have been focused upon recovery of SCFA from WAS recently [11–13].

Anaerobic digestion is composed of three steps: hydrolysis, acidification and methanogenesis [14]. The complex insoluble organic matters were firstly hydrolyzed into small molecules by a variety of microbes secreting different hydrolytic enzymes such as protease, cellulose, amylase and lipase. Thereafter, the hydrolyte is further converted to SCFA rapidly owing to the performance of acid-producing bacteria. The produced SCFA is then utilized by methanogens to generate methane when a proper operational condition is provided [10]. It is believed that the limited yield of SCFA mainly results from the low hydrolysis rate of WAS and the rapid consumption by methanogens. The methanogenesis could be suppressed by regulating the sludge retention time since hydrolytic and acid-producing bacteria are growing about 10 times faster than methanogens [15]. Hence, the hydrolysis of complex organic matters remains a major problem [16]. Many pretreatment methods (e.g. physical, chemical and biological methods) have been studied to enhance SCFA production by improving the hydrolysis process of WAS. Previous studies have shown that chemical pretreatment could significantly disintegrate the flocs of WAS and thus improve the performance of anaerobic digestion [17].

It is well known that ferrate (VI) is a strong oxidant especially in acidic solutions. The ferrate was reported to react with (in)organic matters adopting two-electron or one-electron transfer mechanisms [18]. It could be used as a disinfectant for potable water treatment without production of disinfection byproducts. Apart from the potable water, ferrate could also be used for wastewater or trade effluent treatment with the ability to degrade varieties of pollutants. Moreover, its flocculation property has contributed a lot to the removal of nutrition and hazardous compounds as well. Therefore, ferrate has recently attracted growing interests as a green water treatment chemical, and considerable efforts have been devoted to water treatment by ferrate in pilot scale [19]. Given all these properties, ferrate is supposed to own the ability to dissolve the WAS aggregates and accelerate the hydrolysis step. However, little attention has been focused on the pretreatment of WAS by ferrate. Several researchers reported that the potassium ferrate pretreatment was feasible for sludge disintegration, and it would enhance sludge settleability slightly but was detrimental to the filterability of sludge [20–22]. Whereas, none of these studies have related the system variations (especially microbial community variations) caused by ferrate to the final SCFA production after anaerobic digestion. Therefore, more works should be done to illustrate exactly how the ferrate benefits the SCFA production from WAS.

This study investigated the feasibility of ferrate pretreatment, which

was rarely studied, for facilitating SCFA production from WAS. Potassium ferrate (K_2FeO_4) was chosen to study the effect of ferrate pretreatment on performance improvement of anaerobic digestion in this literature. Firstly, the variations of sludge traits were investigated by analyzing the concentration of soluble chemical oxygen demand (SCOD), extracted extracellular polymeric substance (EPS) and nutrition substance (phosphate and ammonia nitrogen). Then, the effect of ferrate pretreatment on SCFA production at different dosages was explored. And the relationship between extractable EPS and the final SCFA was established afterwards. Finally, the microbial community changes were further studied to elucidate the underlying relationship between biodiversity, population distribution evenness and the anaerobic system performance. To our knowledge, this is the first study revealing details about how ferrate pretreatment improves the SCFA production from WAS. The findings obtained in this study were expected to not only provide a new pretreatment method for WAS digestion but also inspire other researchers and engineers to develop practical strategies for WAS management.

2. Material and methods

2.1. Source of WAS

The wasted activated sludge (WAS) used here was obtained from the secondary sedimentation tank of a full-scale municipal wastewater treatment plant in Harbin, China. The sludge was concentrated by settling at 4 °C for 12 h. Its main characteristics are as follows: pH 6.8 ± 0.1 , total suspended solids (TSS) $23,465 \pm 113$ mg/L, volatile suspended solids (VSS) $15,100 \pm 71$ mg/L, total chemical oxygen demand (TCOD) $13,606 \pm 327$ mg/L, soluble chemical oxygen demand (SCOD) 343 ± 63 mg/L.

2.2. Experiment set up

The pretreatment was performed in six identical beakers and each was fed with 500 mL WAS. Then, 0 (as control), 0.1, 0.3, 0.5, 0.7, 0.9 g/g VSS of potassium ferrate were added into these six beakers, respectively. The sludge was stirred at 300 rpm at ambient temperature for 5 min and then 120 rpm for 40 min based on previous study [21,22]. 400 mL suspension sludge of each beaker was transferred into a corresponding serum bottle with a working volume of 500 mL after 60 min's standing to minimize the influence of remaining ferrate. 40 mL of seed sludge was added into each bottle as an inoculum. The seed sludge was obtained from an anaerobic reactor, which performed steadily on SCFA production, in our laboratory. All six bottles were flushed with nitrogen to eliminate oxygen and capped with rubber stoppers. Then, the bottles were placed in an air-bath shaker (135 rpm) at 35 ± 1 °C. The digestion lasted for 8 d. Three replicates of each experimental condition were performed to ensure the accuracy of the results and the average values were reported. The characteristics of seed sludge are as follows: pH 6.1 ± 0.1 , TSS $22,190 \pm 186$ mg/L, VSS $16,413 \pm 73$ mg/L, TCOD $14,625 \pm 114$ mg/L, SCOD 1850 ± 89 mg/L.

2.3. Analysis of disintegration of EPS and cell envelope

EPS (extracellular polymeric substance) extraction of the sludge was implemented complying with the heat extraction method reported by Li et al. [23]. 50 mL of sample was first centrifuged at 4000g for 5 min. Then, the sludge pellet was resuspended by 15 mL 0.05% NaCl solution. The mixture was diluted with NaCl solution (preheated to 70 °C before use) to its original volume. Afterwards, the suspension was immediately sheared by a vortex mixer for 1 min, and centrifuged at 4000g for 10 min. The supernatant was regarded as loosely bound EPS (LB-EPS). The sludge pellet was resuspended again as before. The suspension was heated to 60 °C in water bath for 0.5 h. Then, the mixture was

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