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Comparison of effects of ferric nitrate additions in thermophilic, mesophilic and psychrophilic aerobic digestion for sewage sludge

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ABSTRACT

The effects of ferric nitrate additions in thermophilic, mesophilic and psychrophilic conditions were investigated in aerobic digestion for sewage sludge. The results showed that the addition of chemical could significantly enhance the volatile solid (VS) removal by shortening 7 days of stabilization time, and increasing 5.52% and 2.12% after 21 days of digestion at 55 °C, 35 °C and 15 °C comparing to the control, respectively. Higher efficiency of removing excessive volatile fatty acid (VFA) was achieved at higher temperature of digestion with ferric nitrate, which resulted in the different orders and changing tendencies of individual VFA. Thus, greater rate of biodegradation of organic substances and higher level of stabilization were obtained for sludge with ferric nitrate at higher temperature, with lower total chemical oxygen demand and soluble chemical oxygen demand. Acceleration of protein disintegration with higher pH, and lower oxidation reduction potential but lower total phosphorus was also acquired by addition of ferric nitrate. VS concentration with chemical is well fitted by an exponential decay function over a temperature range of 15–55 °C, which represented that the improvement of stabilization of sludge with ferric nitrate was almost independent of temperature, but the chemical itself.

1. Introduction

Sewage sludge is an inevitable by-product of wastewater treatment processes, and comprised of organic and inorganic matters as well as a microbial consortium, held together in a matrix formed by extracellular biopolymers and cations [1]. Due to the high contents of water and putrescible organic matters, treatment of the sewage sludge, prior to final disposal, is extremely urgent for wastewater treatment plants (WWTPs), especially for the increasing production of sewage sludge and strict legislations in recent years. However, treatment and disposal of sludge require numerous expenditure, and it usually account for 40–60% of WWTPs' operating costs [2]. Aerobic digestion and anaerobic digestion are two commonly biological technologies applied in most WWTPs. Although anaerobic digestion is devoted to recovery of useful resources in sludge, it maintains lots of insufficiencies of biological methods, such as slow and partial stabilization of sludge, occupation of large land space, *etc.* [3]. But aerobic digestion is acknowledged as a practical technology for rapid stabilization and deep mineralization (great degree of humification) [1] of sludge, normally for medium- and small-sized WWTPs [4].

Generally the aerobic digestion is divided into three systems according to the realm of digestion temperature, such as thermophilic aerobic digestion (45–60 °C, TAD), mesophilic aerobic digestion (25–40 °C, MAD) and psychrophilic aerobic digestion (lower than 20 °C, PAD) [5]. Latterly the TAD has been popular for its fast hydrolysis and degradation of organic substances, either as a pretreatment for enhancement of mesophilic anaerobic digestion and the methane production [2,6], or as a high efficient processing technology independently, particularly like the autothermal thermophilic aerobic digestion (ATAD) [4]. Because that fermentation of waste activated sludge (WAS) was found highly temperature-dependent [7], and thermophilic pretreatments at higher temperatures (>55 °C) and longer operating times (>12 h) yielded higher soluble chemical oxygen demand (CODs) but had a negative effect on the methanogenic activity [8], it made sense to adopt the TAD as a pretreatment for mesophilic anaerobic methane production. Nevertheless, the procedure of MAD was also applied in process of methane production of mesophilic anaerobic digestion [9], because greater solubility of protein could be obtained under aerobic digestion than that under anaerobic digestion, which was better for degradation efficiency during hydrolysis process [1]. Besides, lots of researches had also been done on the operation

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Table 1
Properties of initial sludge employed in simulated one-stage ATAD process.[a]

Parameter	pH	TS (g/l)	VS (g/l)	SCOD (mg/l)	TN (mg/l)	NH_4^+-N (mg/l)	TP (mg/l)
Value	6.45 ± 0.05	48.8 ± 0.3	37.1 ± 0.3	810 ± 10	47 ± 2	35 ± 1	46 ± 2

[a] SCOD – soluble chemical oxidation demand; TN – total nitrogen in supernatant; TP – total phosphate in supernatant; Average data and standard deviation obtained from three tests.

of the MAD as a single unit, like the capability of elimination of *Salmonellatyphimurium* [10]. As for study of PAD, barely a few but was indispensable were reported, such as in temperate regions with various operating temperature in WWTPs due to climate conditions [11]. That was why some researches had been focus on the PAD [11–13]. In view of the low bacterial activity at low temperatures posed a difficulty in reducing or utilizing WAS in cold weather regions and/or during the winter season, a practical method of using isolated strains of *Pseudomonas* and *Aeromonas* species was endeavored under aerobic condition. The reduction rate showed 2- to 8-fold improvement at the temperature range from 4 °C to 15 °C with produced protease and lipase for sludge degradation even at low temperatures [14].

In consideration of aerobic digestion as the integral part of biological technology utilized in WWTPs, plenty of efforts had been devoted in its optimization and innovation. For example, solving problems of ammonia inhibition [15] and foaming and deterioration of dewatering [16] in the ATAD system, ethylene diamine tetra acetic acid (EDTA) on Extracellular polymeric substance (EPS) removal for enhancing MAD of waste activated sludge tailed with bacterial enzymatic pretreatment [17] and hybrid microwave–alkali pretreatment [3], application of specific microbes in PAD as mentioned above, *etc*. However, there were still lots of spaces we could improve. Recently, the introduction and utilization of ferric nitrate in ATAD system had found to be a useful approach, concerning the significant improvement in stabilization of sludge by shortening stabilizing time of about 1/3 [18].

Nevertheless, the application of ferric nitrate is limited to date. Its effects on MAD and PAD are still unknown. Therefore, the chemical approach of conditioning by ferric nitrate would be introduced in MAD and PAD in this study, and a comparison would also be made among corresponding effects of ATAD, MAD and PAD. In addition to, a kinetic equation was proposed to represent the biodegradation of organic matters under chemical coordination.

2. Methods

2.1. Sewage sludge sample

In this study, sewage sludge was collected from a secondary sedimentation tank of a municipal WWTP named Minhang in Shanghai, China. Anaerobic–anoxic–aerobic process is applied in the plant for treating wastewater of 20,000 m^3 per year. The sewage sludge sampled was first going through screening to clear out particles of size greater than 0.5 mm. Then the sludge of about 5% total solid (TS) was obtained by centrifugation at 2200 g for 3 min [4]. The main characteristics of raw sludge were shown in Table 1.

2.2. Startup of the digestion process

Batch experiments were carried out in six tempered glass cylinders of 200 mm (D) × 400 mm (H) with available volume of 4 l each. The profile of the digester was a cylinder of double layers, inside which was containing heating or cooling water circulating between the reactor and a water bath. The temperature conditions of digestion reactions in two groups were set to rise from 35 °C to 55 °C, controlled by a water bath at a rate of 5 °C per day. Then the temperature stayed at 55 °C for another 17 days until the end. The temperature conditions in pairwise digesters of the other four groups were set invariably at 35 °C and 15 °C, respectively. Aeration was supported continually at a rate of 0.13 l/min [19], meanwhile a constant rate of stirring of 120 resolutions was provided [15].

Table 2
Designation of the operating conditions of the different reactors.

Designation	Content
R1	The digester with $Fe(NO_3)_3$•$9H_2O$ dosed at 55 °C
R2	The digester without $Fe(NO_3)_3$•$9H_2O$ dosed at 55 °C
R3	The digester with $Fe(NO_3)_3$•$9H_2O$ dosed at 35 °C
R4	The digester without $Fe(NO_3)_3$•$9H_2O$ dosed at 35 °C
R5	The digester with $Fe(NO_3)_3$•$9H_2O$ dosed at 15 °C
R6	The digester without $Fe(NO_3)_3$•$9H_2O$ dosed at 15 °C

The whole process of digestion reaction lasted for 21 days. The operating conditions of the different reactors were designated as those showed in Table 2. The $Fe(NO_3)_3$ of dosage of reducing 1000 mg/l acetic acid [20] was added on 6th day [21] with pH adjusted to 6.5 [22] for R1, R3 and R5. The decreased amount of sludge by sampling was taken into account when the chemical reagent was added into the reactors on 6th day. $Fe(NO_3)_3$ was put into digester 6 h before sampling on 6th day, for the sake of adequately reaction between $Fe(NO_3)_3$ and sludge. All experiments were conducted triplicated, and all of indicators were determined in triplicate and the standard deviations were achieved.

2.3. Chemical analysis

Volatile solids (VS) and total solids (TS) were measured according to the Standard Methods [23] with values brought in by chemical reagents subtracted. The pH was determined by a pH meter (pHs-3C, Lei ci Co. Ltd., Shanghai) and the oxidation reduction potential (ORP) was monitored by an ORP meter (ORP-502, Ruosull Technology Co., Shanghai, China). Total chemical oxidation demand of sludge (TCOD) was measured by the standard reflux titrimetric method [24]. The sludge sampled was centrifuged at 12,000 g for 5 min before filtration through a 0.45 µm mixed cellulose ester membrane. The filtrate was analyzed for determination of soluble chemical oxidation demand (SCOD), NH_4^+-N, total nitrogen (TN), total phosphate (TP) according to the Standard Methods [23]. The filtrate mixed with 3% H_3PO_4 (to adjust the pH of the filtrate holding at round 4.0) was injected into a Shimadzu GC-2010 gas chromatograph, which was equipped with a flame ionization detector and DB-FFAP column (30 m × 0.25 mm × 0.25 mm), in order to obtain the level of VFA according with method of Chen et al. [25]. The content of VFA was expressed as COD of mg/l by modification with the influence of H_3PO_4 involved. The software of SPSS in version 19.0 for Windows (SPSS, IBM) was used for statistical analysis and statistically significant correlations were determined at a confidence interval of 95% ($p < 0.05$; Tukey's test).