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Determination of the optimal dosing time of ferric nitrate on disinhibition of excessive volatile fatty acids in autothermal thermophilic aerobic digestion for sewage sludge

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Ferric nitrate has been proved to be effective on removing inhibition of excessive volatile fatty acids (VFAs) and promote stabilization of sludge in autothermal thermophilic aerobic digestion (ATAD) recently. The dosing time of $Fe(NO_3)_3$ had a significant impact on performance of $Fe(NO_3)_3$ on disinhibition of excessive VFAs in the ATAD process. The timings of $Fe(NO_3)_3$ additions were determined as 3rd day, 6th day, 9th day and 12th day to remove available acetic acid. The lowest concentrations of total VFAs (TVFA) and VFAs but highest microbial activity were found in the digester with $Fe(NO_3)_3$ dosed on the 6th day (T6). The sludge in T6 achieved stabilization 6 days earlier than that in digester without chemical addition with VS removal of 38.50% on the 15th day and VS removal of 42.74% on the 21st day. The lower TVFA concentration favored the lower NH_4^+-N and TN contents and improved the microbial activity which contributed to the lower concentrations of SCOD and TP in supernatant.

1 Introduction

Stabilization of sludge to kill pathogens and eliminate putrescible organic pollution prior to its disposal is indispensable for the management of the sewage sludge. The increasing legislative constraints for sludge disposal have made it impending for wastewater treatment plants (WWTPs) to seek for new developments. [1] Especially, for the medium- and small-sized WWTPs with restricted scale of land, the autothermal thermophilic aerobic digestion (ATAD) process has been popular for its small occupied area in Europe and North American since the early 1970s.[2] The ATAD process has been acknowledged for its efficient pathogen inactivation, high volatile solids (VS) reduction capability, low energy consumption and simple control requirements.[3] Meanwhile, numerous progresses in optimization and adaptation of ATAD technology have been achieved.[4]

Nevertheless, the concerns about issues of poor dewaterability, foaming, disadvantageously excessive concentrations of ammonia and volatile fatty acids (VFAs) generating in the ATAD process for sewage sludge still existed.[5-7] Especially, the superfluous VFAs concentration in ATAD system causing by limited aeration and retention time as well as high waste load have aroused more and more attentions.[8-10] Although the VFAs are most important intermediary substances for microorganisms[11] and drawn great interests in applications of producing biodegradable plastics, bioenergy and biological nutrient removal processes,[12] the product inhibition resulted from the accumulation of VFAs should be taken into consideration in acidification process.[13] Inhibition of a combination of VFAs containing 2–6 carbon atoms each with threshold of VFA concentration of 17 ± 1 g COD_{VFA} L^{-1} and acetate

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being approximately 50% as inhibitory as the other organic acids were shown in fermentation of pre-treated waste activated sludge.[13] The overmuch generation of VFAs also makes the hydrogen production process unfavorable by limiting the substrate degradation, which is much important in acidogenic process.[14]

Oxygen is always insufficient in the ATAD system, especially in the initial stage with abundant organic matters, which was due to the limited aeration rate for self-heating through restricting the loss of heat in water evaporation and air effluent.[15] Hence, when the oxygen, as the terminal electron acceptor, along the respiratory chain is limited under micro-aerobic condition, the metabolic pathway of substrate to acetate is strengthened in order to maintain the balance between nicotinamide adenine dinucleotide (NADH) and NAD^+ as well as adenosine triphosphate (ATP) production maximization.[16] However, the conversion route of propionic acid to acetic acid would be hindered once the acetate accumulated over high because that the propionic acid is more advantageous to the oxidation of NADH-H than the butyrate acid.[17,18] As the concentration of total VFAs (TVFA) arrives 5000mg COD_{VFA} L^{-1} with propionic acid content of over 1000 mg COD_{VFA} L^{-1}, the Gram-positive bacteria is suppressed distinctly, which is dominant bacteria in ATAD system.[19,20] Therefore, focus should be taken on the establishment of methodology to decrease VFAs levels in ATAD system. Usage of ferric nitrate was confirmed to be a feasible method to remove the inhibition of excessive VFAs and enhance the efficiency of sludge stabilization in one-stage ATAD process lately.[7] Optimal dosage of ferric nitrate on disinhibition of superfluous VFAs in one-stage ATAD system was also definite.[21] However, the proper dosing time of ferric nitrate is not determined until now.

The purpose of this study was to ascertain the optimal timing of ferric nitrate that added in the batch experiments due to the uncertain point of time when VFAs over-produced in the ATAD process. The effects of ferric nitrate on removing VFAs and microbial activity as well as sludge stabilization at different dosing time were investigated in this work.

2 Experimental

2.1. Sewage sludge sample

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

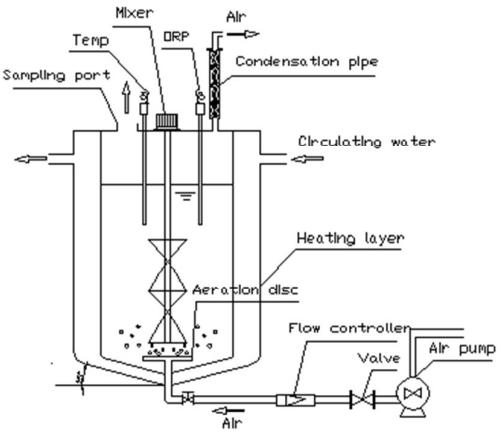
Parameter	pH	TS (g/L)	VS (g/L)	SCOD (mg/L)	TN (mg/L)	NH_4^+-N (mg/L)	TP (mg/L)
Value	6.57 ± 0.05	55.1 ± 0.3	40.0 ± 0.2	3400 ± 30	313 ± 15	105 ± 8	204 ± 11

[a] SCOD, soluble chemical oxidation demand; TN, total nitrogen in supernatant; TP, total phosphate in supernatant.

In this study, sewage sludge was sampled from a secondary sedimentation tank of a municipal wastewater treatment plant (WWTP) in Shanghai, China. This WWTP possesses an anaerobic–anoxic–aerobic process with a capacity of 45,000 m^3 wastewater treatment daily. The raw sludge collected was preserved at 4 ± 1 ℃ to maintain freshness prior to use after screened out dross of granule diameter > 0.5mm and centrifugation at 3000 g for 3 min to obtain a total solid (TS) concentration between 5% and 6%.The initial properties of sludge were shown in Table 1.

2.2. Startup of the ATAD process

Five simulated one-stage autothermal thermophilic aerobic digesters were set up to conduct the batch experiments. The body of the digester was tempered glass cylinder of 200 mm (D) × 400 mm (H), equipped with 5 L available volume (as shwon in Fig. 1). A circulatory water bath was installed to create a circumstance of temperature rising from 35℃ to 55℃ and constant temperature environment subsequently. Aeration was supplied ceaselessly with an air flow rate of 0.033 L gas L^{-1} sludge h^{-1} through microporous diffusers. A constant stirring rate of 110 revolutions per



Fi. 1. Schematic diagram of the simulated one-stage ATAD digester

minute was affiliated. A cooling water system was set up to recover water vapor in exhaust throughout the whole period of digestion process. The pH in the digestion process was not regulated.

The whole digestion process took 21 days and samples were taken at particular intervals for analysis. As the VFAs concentration achieved a peak level on the 9th day in one-stage ATAD process,[7] chemicals were added on the 3th, 6th, 9th,12th day of ATAD process with designed dosages 6 hours before sampling, respectively, for the sake of adequate reactions between chemical reagents and sludge. The dosage of $Fe(NO_3)_3 \cdot 9H_2O$ was 3.16 g per L sludge, which was calculated at the ideal molar ratio of 1:3 in order to form $Fe(CH_3COO)_3$ to reduce acetic acid of 1500 $mg \cdot L^{-1}$ with the decreased amount of sludge by sampling counted.[7] Defined amounts of sodium hydroxide were added into digesters in order to eliminate the influence of chemicals additions on pH. The dosing time of the different treatments were 3rd day (T9), 6th (T6), 9th (T9) and 12th (T12), respectively, and the one without $Fe(NO_3)_3$ dosed was designated as the control (T0).

1.3. Analytical methods

VS and TS were measured according to the Standard Methods[22] with values result from $Fe(NO_3)_3$ input eliminated. The pH was determined by a pH meter (pHs-3C, Lei ci Co. Ltd., Shanghai). The sampled sludge was centrifuged at 12,000g 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) and total phosphate (TP) according to the Standard Methods.[22] The filtrate was mingled with 3% H_3PO_4 to keep pH at approximately 4.0 before analysis of volatile fatty acids (VFAs). The VFAs concentrations were measured by a Shimadzu GC-2010 gas chromatograph with a flame ionization detector and DB-FFAP column (30 m × 0.25 mm × 0.25 mm) in accordance with the method by Chen et al.[23] The content of VFAs was expressed in mg/L as COD.

The measurement of adenosine triphosphate (ATP) content in sludge was based on the following reaction (1):

$$ATP + D\text{-}luciferin + O_2 \rightarrow oxyluciferin + PPi + AMP + CO_2 + light \quad (1)$$

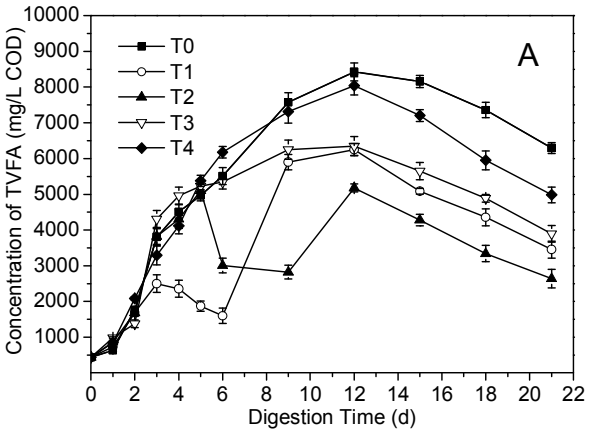
Sludge sample was extracted to centrifuge at 12,000 g for 15 min. The residual sludge was washed with PBS (0.1 M phosphate buffer solution, pH 6.9) three times before mixing with ultrapure water using ultrasonic processing in room temperature for 5 min to be uniform. The sample was preserved at 4 ℃ for 12 h before going reaction with luciferase (Bac Titer-Glo microbial cell viability assay, Promega Corp.), which was measured as a Relative Luminescence Unit (RLU) in a Spectra Max L microplate luminometer (Varioskan Flash, Thermo Corp.). The pH-optimum of reaction is 7.75 and the resulting green light has an emission maximum at 562 nm.[24,25]

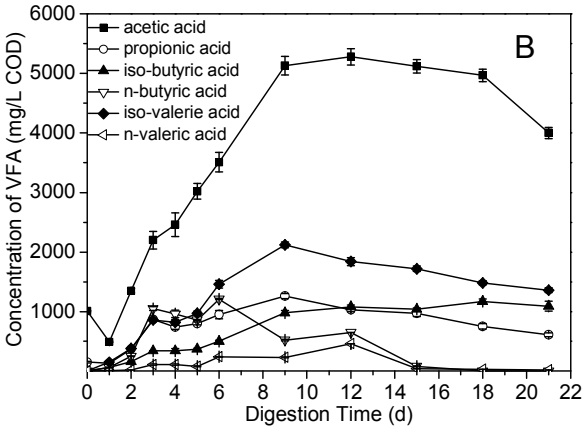
All of the indicators were determined in triplicate and the standard deviations were obtained. Statistical analysis was carried out using the software SPSS version 19.0 for Windows (SPSS, IBM). The correlations were considered statistically significant at a 95% confidence interval ($p < 0.05$; Tukey's test).

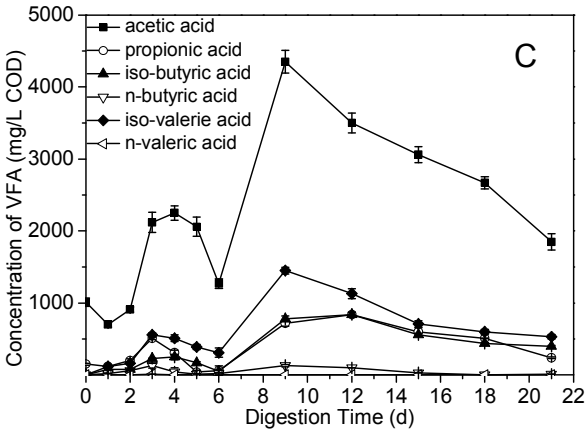
3 Results and Discussion

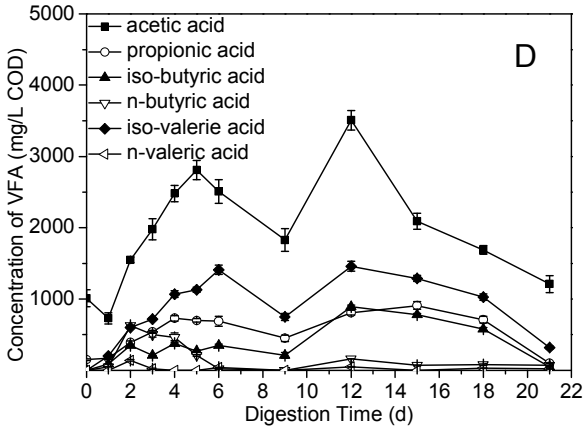
3.1 Effects of different dosing time on TVFA and individual VFA in one-stage ATAD system

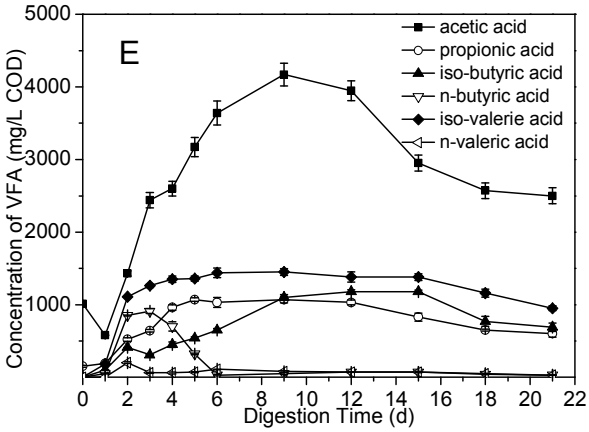
The total volatile fatty acids (TVFA) included acetic acid, propionic acid, n-butyric acid, iso-butyric acid, n-valeric acid and iso-valeric acid. As shown in Fig. 2A, there were no obvious differences of the TVFA concentrations among the five treatments in the first two days ($p<0.05$). The TVFA concentrations of all five digesters had reached maximum levels on the 12th day, which were a little later than that reported by Liu et al.[26] The TVFA content in T0 was continually increased to 8428 mg/L on the 12th day, then declined to 6239 mg/L at the end of digestion (much more than 5000 mg/L),











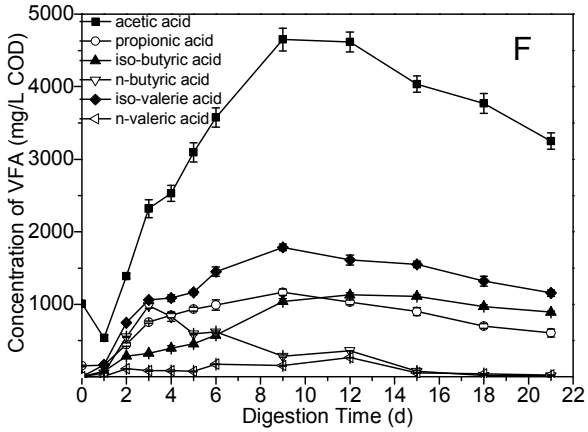


Fig. 2. Variations of (A) TVFA (total VFAs) in supernatant of simulated one-stage ATAD system; (B) different species of VFA in supernatant of T0; (C) different species of VFA in supernatant of T3; (D) different species of VFA in supernatant of T6; (E) different species of VFA in supernatant of T9; (F) different species of VFA in supernatant of T12.

which would still cause inhibition of microbial activity.[19] The increment of TVFA value in the initial stage of T0 should be due to the microaerobic and thermophilic condition[27,28] and the decrease afterwards should be the consequence of thermophile bacteria metabolism.[27] However, differences appeared in other four digesters with chemicals additions. A sharp fall of TVFA concentration had both happened to T3 and T6 on the 3rd day and the 6th day after $Fe(NO_3)_3$ dosed, respectively, while those in T9 and T12 were just slow down the rising rate when the chemicals added comparing to that in T0. The decrease of TVFA concentration in T6 was much more notable from 3003 mg/L on the 6th day to 2821 mg/L on the 9th day, which were 2506mg/L and 4753 mg/L lesser than those in T0, respectively. Compared with those reductions in T6, the decline of TVFA content in T3 was slighter with 1302 mg/L on the 3rd day and 3912 mg/L on the 6th day lower than those in T0, respectively. The peak level of TVFA in T6 was 5180 mg/L on the 12th day with 3248 mg/L lesser than that in T0 while that in T3 was 2177 mg/L. The TVFA content in T6 ended up with 2639 mg/L which was 3654 mg/L lower than that in T0 while that in T3 was 2842 mg/L. As for TVFA levels in T9 and T12, the decreases were between those of T0 and T6. In addition, as seen in Fig. 2A, the TVFA content in the stimulated one-stage ATAD process was just over 5000 mg/L by 6 days digestion, which would induce the inhibition of VFAs in ATAD system.[19] Moreover, the TVFA in T6 had not exceeded 5000 mg/L after chemical addition while other three processing groups

had all achieved more than 5000 mg/L TVFA level after $Fe(NO_3)_3$ dosed. Thus, it could be concluded that the most effective disinhibition of TVFA could be obtained in digester T6 with optimal dosing time of $Fe(NO_3)_3$.

The variations of individual VFA in T0 to T12 were shown in Fig. 2B to Fig. 2F, respectively. Fig. 2B showed that the higher two kinds of VFAs were acetic acid and iso-valeric acid, which was in accord with the results of Xu et al.[25] The content of iso-valeric acid was higher than that of propionic acid in thermophilic condition, which coincided with the report by Hao and Wang,[28] indicating that protein was the main substrate except carbohydrate during these digestion processes.[23] The acetic acid content in T0 was as high as 5280 mg/L on the 12th day and ended with 4000 mg/L on the 21st day. However, the variations of individual VFAs in other four digesters were similar to the trends of TVFA, respectively. As shown in Fig. 2D, the acetic acid content in T6 decreased after $Fe(NO_3)_3$ dosed on the 6th day and got to 1830 mg/L on the 9th day, which was 3300 mg/L lower than that in T0, considering that the possible mechanism of reactions (2) to (5) demonstrated in previous research by Jin et al.[7]

$$Fe^{3+} + 3CH_3COO^- \rightleftharpoons Fe(CH_3COO)_3 \quad (2)$$

$$Fe(CH_3COO)_3 + 2H_2O \rightleftharpoons Fe(OH)_2(CH_3COO) + 2CH_3COOH \quad (3)$$

$$2Fe(OH)_3 + 2HNO_3 + 2HCOOH + 2CH_3COOH \rightarrow Fe_2(HCOO)_2(CH_3COO)_2(NO_3)_2 + 6H_2O \quad (4)$$

$$Fe_2(HCOO)_2(CH_3COO)_2(NO_3)_2 + H_2O \rightarrow Fe_2(HCOO)_2(CH_3COO)_2(OH)(NO_3) + HNO_3 \quad (5)$$

Then the level of acetic acid in T6 increased to the top of 3510 mg/L on the 12th day in consideration of the continually degradation of matrix.[29] There were 1770 mg/L lower comparing the maximum level of acetic acid in T6 with that in T0 on the 12th day and 2790 mg/L at the end of digestion. The acetic acid concentration in T3 was showed in Fig. 2C. The decline of acetic acid value was one day delayed after chemical added on the 3rd day, which should attribute to the violent releasing and metabolism of macromolecules in the initial stage of ATAD process.[27] The decrease caused by chemical addition ended on the 6th day with 1270 mg/L, which was 2240 mg/L lesser than that in T0. Similar to that happened in T6, the acetic acid level in T3 rose again to the peak on the 9th day with 4350 mg/L, which was only 780 mg/L lower than that in T0. Nevertheless, the time of the maximum value of acetic acid obtained in T3 was advanced, which should be due to the early over consumption of organic matters in view of the disinhibition of excessive VFAs. The end of acetic acid level in T3 was 1850 mg/L, which was 2150 mg/L lesser than that in T0. The acetic acid levels in T9 and T12 also declined after chemical additions. The variations of acetic acid contents in T9 and T12 were between those in T0 and T6. In a word, the chemical of $Fe(NO_3)_3$ had played an important role in removing available acetic acid, which could decreased the TVFA content, especially for T6 digester with optimal timing of chemical addition.

3.2 Microbial activity and VS removal at different dosing time in one-stage ATAD system

Adenosine triphosphate (ATP) content measured in luciferin-luciferase enzyme system has been utilized to access the general physiological activity.[24] The variations of ATP concentrations were shown in Fig. 3A. There were no obvious differences of the ATP contents among the five treatments on the 1st day ($p<0.05$). The ATP content in T0 declined all the way through the whole digestion except for a little fluctuation between 3rd day and 5th day, which tallied with the result by Yuan et al.[30] The ATP levels in other four digesters all had rapid increases when the chemical added and then declined until the end of digestion. Especially, the ATP content in T6 still reached up to 3376 relative light Unit (RLU) on the 12th day, 6 days after chemical dosed, which was only 97 RLU lesser than that in T3 on the 3rd day but 579 RLU higher than that in T12 on the 12th day.The ATP value in T9 was 2335 RLU, nevertheless, the ATP level in T0 was only 969 RLU on the 12th day and 448 RLU on the 19th day, which was more than 200 RLU lower comparing with other four processing groups. These results manifested that the dosing time of 6th day maintained the highest microbial activity which should be due to the best control of TVFA concentration under inhibition level.

The ATAD process has a quick sludge reduction rate under thermophilic conditions. As shown in Fig. 3B, the VS removal of T0 could reach 38.28% (>38%) on the

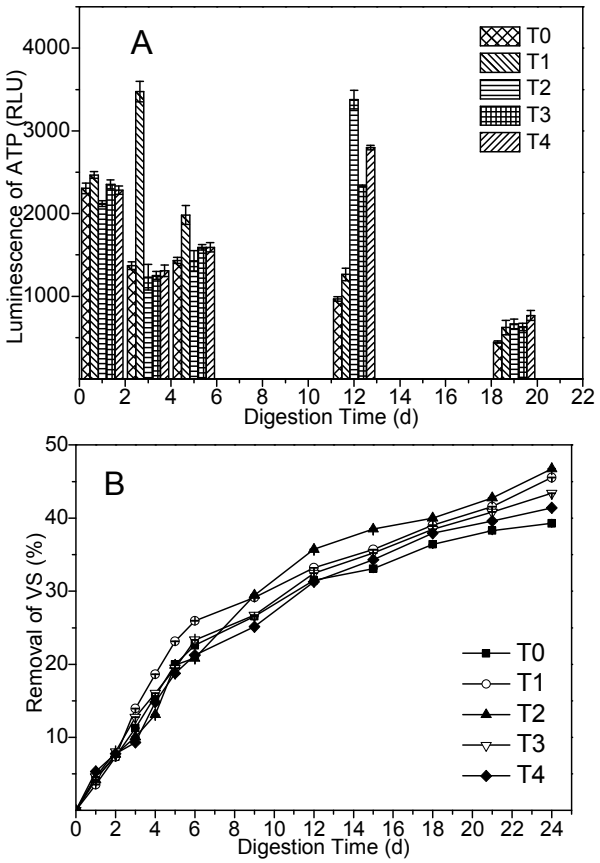
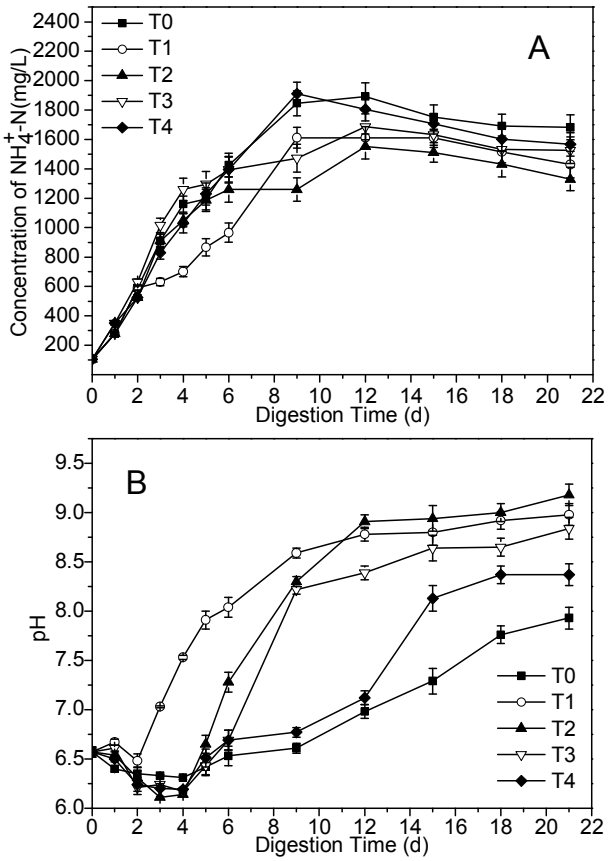


Fig. 3. Variations of (A) ATP concentrations in sludge and (B) VS removals in supernatant at different dosages in one-stage ATAD system.

21st day, achieving the EPA Class A requirements for sewage sludge[31] and obtained 39.29% on the 24th day. In the first two days, there were no obvious differences of the sludge digestion efficiencies among the five treatments ($P<0.05$). However, the VS removal efficiency of T3 became faster after $Fe(NO_3)_3$ dosed on the 3rd day. The same conditions also happen to the rest three digesters with chemical additions. The VS removal of T6 had exceeded that of T3 after digestion of 9 days and held the lead among all five digesters until the end of digestion. The VS removal of T6 achieved 38.50% on the 15th day with stabilization 6 days earlier than that of T0 and obtained 42.74% after 21 days digestion. The VS removal of T6 still kept a high rate after digestion of 21 days and reached 46.75% on the 24th day with 7.46% more than that of T0. The sludge in T3 obtained stabilization on the 18th day with 39.06% VS removal and ended with 45.55% VS removal on the 24th day. As for T9 and T12, the sludge in T9 and T12 achieved stabilization on the 18th day and the 21st day with 38.47% VS removal and 39.60% VS removal, respectively. Thus, it could be concluded that the sludge in T6 could obtain both fastest and highest stabilization requirement of all through the ATAD process, which was associated with activity of microbe significantly.[7]

3.3 Effects of different dosing time on NH_4^+-N, pH and TN concentrations in one-stage ATAD system

In the initial stage of ATAD system, the concentration of NH_4^+-N increased vigorously due to the degradation of protein under thermophilic condition.[18] The variations of NH_4^+-N concentration were shown in Fig. 4A. There were no obvious differences of the NH_4^+-N concentrations among the five treatments in first two days ($P<0.05$). The content of NH_4^+-N in T0 increased sharply before the 12th day and obtained the maximum of 1892 mg/L. Then it started to decline slowly and temperately and ended with 1682 mg/L, in view of the balance of production and stripping.[30] The increase rate of NH_4^+-N concentration in T3 began to fall behind after $Fe(NO_3)_3$ added on the 3rd day. The increase rates of NH_4^+-N levels in other three digesters with chemical dosed also slowed down, particularly the change of NH_4^+-N content



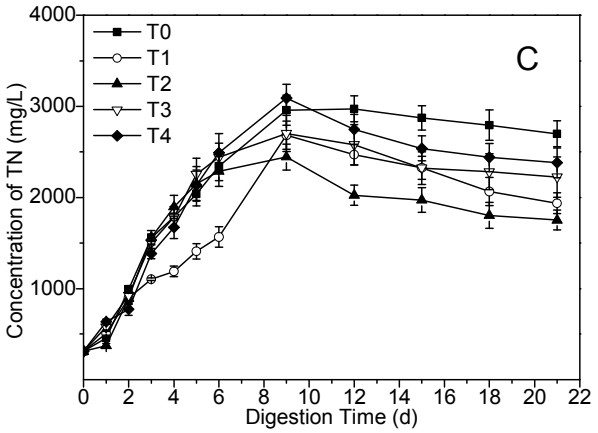


Fig. 4. Variations of (A) NH_4^+-N; (B) pH and (C) TN concentrations in supernatant at different dosages in the one-stage ATAD system.

in T6, which should be due to the decrease of dissolved acidic compounds (VFAs) precipitated by $Fe(NO_3)_3$ and then caused the reduction of the alkaline substances (e.g. NH_3).[7] The maximum values of NH_4^+-N in T6 was 1552 mg/L on the 12th day with 340 mg/L lesser than that in T0 and ended with 1330 mg/L with 352 mg/L lower than that in T0. As for T3, T9 and T12 were 1612 mg/L, 1686 mg/L and 1806 mg/L for the maximums obtained on the 12th day and 1430 mg/L, 1526 mg/L and 1566 mg/L for the end of digestion, respectively.

The variations of pH were shown in Fig. 4B. The pH values in all digesters except for the digester T3 decreased from 1st day to 4th day, which should ascribed to the acidification of matrix.[18] The changes of pH values in digesters with chemical additions comparing with that in T0 were opposite to those of NH_4^+-N contents. As seen in Fig. 4A, the increase rates of NH_4^+-N levels in digesters with $Fe(NO_3)_3$ dosed were lower comparing with that in T0 when chemicals added. Nevertheless, the increase rates of pH values in digesters with $Fe(NO_3)_3$ dosed were higher comparing with that in T0 when chemicals added. These results should be due to reason that pH was influenced by releasing of ammonia nitrogen as well as acid-base Balance.[18] The pH values of all digesters were between 6.0 and 9.5. The maximum value of pH was achieved in T6 with 9.18 on the 21st day and the pH level in T0 was 7.93 at the end of digestion.

The variations of TN levels were similar to those of NH_4^+-N levels under thermophilic condition in consideration that nitrification and denitrification were inhibited.[18] As seen in Fig. 4C, the increase rates of TN concentrations in digesters with chemical additions declined comparing with that in T0 when $Fe(NO_3)_3$ were dosed. There were no obvious differences of the TN concentrations among the five treatments in first two days ($P<0.05$). The TN content in T0 increased sharply to 2973 mg/L on the 12th day and then decreased slowly to 2698 mg/L at the end of digestion. The TN content in T6 obtained minimum value of all with 2443 mg/L on the 9th day, 3 days earlier than that in T0, which should be due to the degradation of protein advanced by enhanced microbial metabolism. Then it declined to 1752 mg/L after digestion of 21 days with 946 mg/L lower than that in T0. The TN levels in other three digesters changed between those in T0 and T6.

3.4 Variations of SCOD concentrations at different dosing time in one-stage ATAD system

Microbial cells rupture and abundant organic matters released into the supernatant would cause the increase of SCOD value in the early stage of ATAD process (0-6 day).[29] As shown in Fig. 5, the variations of SCOD values were much like those of nitrogen levels but the time of maximums obtained advanced for 3 days. There were no obvious differences of the SCOD concentrations among the five treatments in first two days ($P<0.05$). Afterwards, the SCOD content in T3 increased slower than other four processing groups for chemical addition on the 3rd day and reached highest with 24703 mg/L on the 6th day. The SCOD levels in other three digesters with chemical additions did not increase again after $Fe(NO_3)_3$ dosed. Especially, the SCOD content in T6 had achieved the maximum value of 26437 mg/L on the 5th day, which was four days advanced comparing with that in T0 with 27914 mg/L

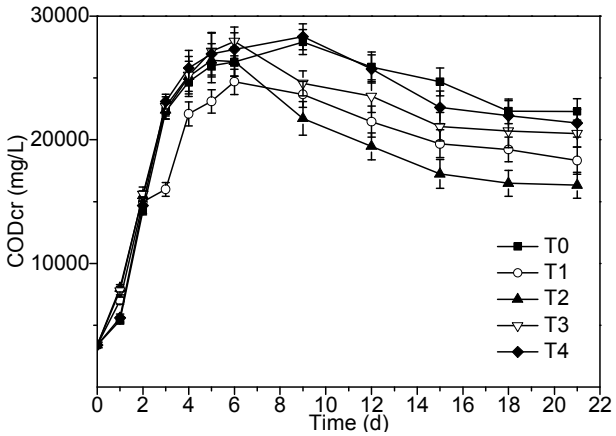


Fig. 5. Variations of SCOD concentrations in supernatant at different dosages in one-stage ATAD system.

on the 9th day. The SCOD level in T6 ended with 16335 mg/L while that in T0 was 22295 mg/L at the end of digestion process. The SCOD concentrations in other three digesters changed between those in T0 and T6 after 9th day. In a word, the dosing time of 6th day was the most reasonable choice for the removal of SCOD and improvement of performance of one-stage ATAD system.

3.5 Effects of different dosing time on TP concentrations in one-stage ATAD system

The variations of total phosphorus concentrations in the supernatant (TP) during digestion process were shown in Fig. 6. The TP contents in T0 increased sharply in the initial stage of 5 days, in consideration of that some phosphorus released from rapid cell lysis of thermolabile microorganisms.[18] The highest amount of TP level in T0 could achieve 1104 mg/L on the 5th day and then fluctuated until the end of digestion with 778 mg/L. As for digesters with chemical additions, the TP contents decreased when $Fe(NO_3)_3$ were dosed. After 21 days digestion, the minimum concentration of TP was obtained in T6, although the dosage of $Fe(NO_3)_3$ was not the maximum. It should be attributed to the highest microbial activity with the maximum production of ATP which utilized the phosphorus[18] and relatively optimal pH obtained for the formation of magnesium ammonium phosphate (*pH=9.5*).[32] As a result, lowest level of TP in supernatant but highest level in sludge could be obtained in T6 due to the isolated circumstance for phosphorus migration.

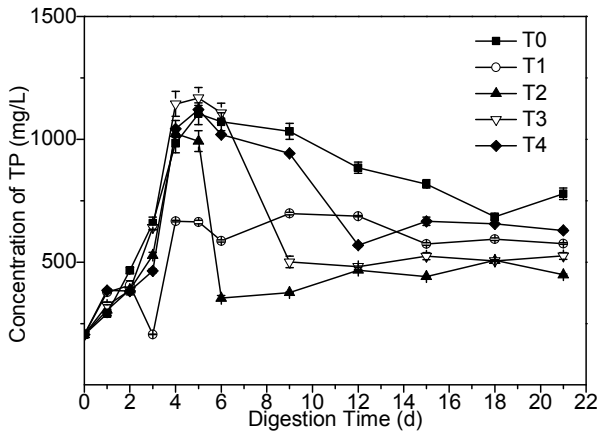


Fig. 6. Variations of TP concentrations in supernatant at different dosages in one-stage ATAD system.

4 Conclusion

Stabilization process of sludge was significantly enhanced by the disinhibition of VFAs in the one-stage ATAD system. VS removal of 38.50% was achieved in digester with $Fe(NO_3)_3$ dosed on 6th day (T6) after digestion of 15 days, which was 6 days earlier than that in digester without addition to achieve stabilization. The lowest concentrations of TVFA and VFAs were found in T6 with the highest ATP content and the TVFA level in T6 was under 5000 mg/L after addition of $Fe(NO_3)_3$. Lowest concentrations of NH_4^+-N, TN and SCOD in supernatant while highest content of TP in digestion sludge were obtained in T6.

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