

Free Ammonia Pretreatment Improves Degradation of Secondary Sludge During Aerobic Digestion

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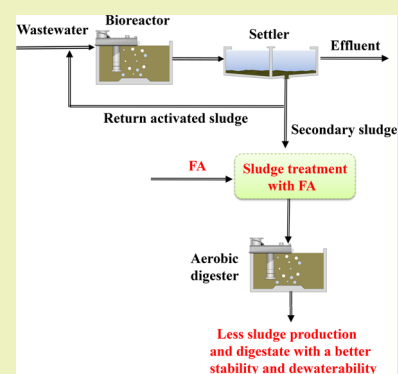
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ABSTRACT: Aerobic digestion is commonly used to achieve secondary sludge reduction in the small-size wastewater treatment plants. Nevertheless, secondary sludge degradation is usually restricted by the slow hydrolysis rate and low degradable percentage of secondary sludge. Here, we present an innovative approach using pretreatment of free ammonia (FA, i.e. NH_3), a renewable chemical from wastewater, to improve the degradation of secondary sludge during aerobic digestion. The secondary sludge was degraded by $36 \pm 4\%$ (volatile solids (VS) basis) within 15 days of aerobic digestion while being pretreated at $300 \text{ mg NH}_3\text{-N/L}$ (pH 9.0; total ammonia nitrogen = 800 mg N/L) for 24 h, whereas only $23 \pm 3\%$ (VS basis) of the secondary sludge without FA pretreatment was degraded over the same period. Similarly, the production of inorganic nitrogen also increased from 27 ± 2 to $38 \pm 2 \text{ mg N/g VS}$ after implementing FA pretreatment, corroborating the idea that degradation of secondary sludge was effectively improved by FA pretreatment. Further analysis by model revealed that the improved hydrolysis rate and increased degradable percentage of secondary sludge were responsible for the enhanced sludge degradation in aerobic digestion. It was also found that FA pretreatment would produce an aerobic digestate with a better stability and dewaterability, as indicated by the lower degradable percentage of digestate and the decrease of capillary suction time from 38 ± 1 to $34 \pm 1 \text{ s}$, respectively. Economic analysis indicates that the FA pretreatment approach would be economically favorable when the sludge transport and disposal cost is higher than $\$40/\text{wet tone}$.

KEYWORDS: Secondary sludge, Aerobic digestion, Free ammonia, Degradation, Dewaterability



INTRODUCTION

Large quantities of excess sludge are produced in the activated sludge system of the wastewater treatment plants (WWTPs) and huge costs are needed for its disposal.^{1–3} Aerobic digestion is a common method for sludge stabilization and reduction prior to its disposal in the small-size WWTPs. Nevertheless, the degradation of secondary sludge in aerobic digestion is usually restricted by the slow hydrolysis rate and low degradable percentage of secondary sludge.⁴ To this end, plenty of sludge pretreatment approaches have been developed to improve secondary sludge degradation, such as mechanical, chemical, biological, and electrical pretreatment.^{5–12} For example, Song et al. reported that the volatile solids degradation increased from 28 to 34% at an aerobic digestion time of 17.5 days after

the sludge was electrochemically pretreated for 30 min at electric power of 5 W.⁵ However, the previously proposed approaches need either large amounts of chemical consumption or intensive energy input, resulting in intensive costs.⁴ Therefore, an alternative approach with a low cost is still required.

Our recent studies have shown that free ammonia (FA, NH_3), a renewable material from WWTPs, is able to enhance the anaerobic degradation of sludge.^{13,14} For example, Wei et al. demonstrated primary sludge pretreatment using FA for 24 h at

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85–680 mg NH₃-N/L could enhance anaerobic methane production by 5–15%.¹⁴ Wei et al. also showed that anaerobic methane generation from secondary sludge could be enhanced by 20–30% under the same FA pretreatment conditions.¹³ Wang et al. demonstrated that the sludge concentration in the mainstream reactor decreased after incorporating FA pretreatment in the sludge recycling line.¹⁵ Furthermore, the FA pretreatment approach was demonstrated to be economic attractive.^{13–15}

These findings allowed us to hypothesize that FA pretreatment on secondary sludge before aerobic digestion could be a potential approach for improving sludge degradation. To confirm this assumption, a secondary sludge was pretreated for 24 h by FA at 300 mg N/L with the secondary sludge without FA pretreatment as the control. An activated sludge was used to aerobically digest these secondary sludges for 15 days, during which the degradations of the secondary sludges with and without FA pretreatment were calculated and compared based on volatile solids (VS) destruction and biomass specific inorganic nitrogen production. Model-based analysis was conducted to reveal the reason for the enhanced sludge degradation by FA pretreatment. The dewaterability of aerobically digested sludge was also evaluated by capillary suction time. Economic evaluation was also performed to shed light on the economic potential of the FA pretreatment approach. This study for the first time evaluated the effect of FA pretreatment on the degradation of secondary sludge during aerobic digestion.

MATERIAL AND METHODS

Sources of Sludge. The secondary sludge and digesting sludge were employed for the following aerobic digestion tests. The secondary sludge was harvested from the return sludge line of a WWTP (sludge retention time = 10 days) with the total solids (TS) and volatile solids (VS) concentrations being 9.2 ± 0.2 and 7.2 ± 0.2 g/L, respectively. Its pH, total chemical oxygen demand (TCOD) concentration, and soluble chemical oxygen demand (SCOD) concentration were 7.1 ± 0.1 , 9.4 ± 0.2 g/L, and 0.2 ± 0.2 g/L, respectively. Digesting sludge was collected from the aerobic unit of the same WWTP with TS and VS concentrations of 4.2 ± 0.2 and 3.3 ± 0.1 g/L, respectively. Its pH, TCOD, and SCOD concentrations were 7.1 ± 0.1 , 4.4 ± 0.2 g/L, and 0.2 ± 0.1 g/L, respectively. The digesting sludge was applied to aerobically degrade the secondary sludge, with the details shown in the section “Aerobic Digestion Experiments”.

Secondary Sludge Pretreatment by FA. Batch experiments were conducted to anaerobically pretreat the secondary sludge using FA. Three batch reactors were used with each reactor having 0.6 L of secondary sludge. One reactor served as an experimental reactor, and the other two served as the control reactors. An ammonium stock solution (80 g/L) was dosed into the experimental reactor to gain a total ammonia nitrogen (TAN, i.e., NH₃-N + NH₄⁺-N) concentration of 800 mg N/L. pH was then controlled at 9.0 ± 0.1 during the 24 h pretreatment period. The FA concentration was determined as 300 mg N/L by the formula $S_{\text{TAN}} \times 10^{\text{pH}} / (K_b / K_w + 10^{\text{pH}})$, in which S_{TAN} is the TAN concentration, K_b is the ionization constant of the ammonia equilibrium equation, and K_w is the ionization constant of water.¹⁶ The K_b / K_w value was determined using the formula $K_b / K_w = e^{6344 / (273 + T)}$ ($T = 25$ °C during this experiment).¹⁶ The FA concentration was chosen based on the findings of a previous study that 300 mg NH₃-N/L was biocidal to bacteria.¹³ It should be highlighted that this was only a proof-of-concept study; therefore, only one set of FA treatment conditions was tested here. In contrast to the experimental reactor, pH was only monitored and not adjusted in the control reactors and was observed as 7.0–7.5. No NH₄⁺-N was added into the control reactors. The two control reactors were the same but

the sludges would be used for different purposes, as detailed in the section “Aerobic Digestion Experiments”. Note that our previous study has demonstrated that pH 9.0 pretreatment cannot enhance sludge degradability. We also demonstrated that NH₄⁺-N pretreatment alone at 800 mg N/L would not improve sludge degradability.¹³ Consequently, no separate control with pH 9.0 pretreatment or NH₄⁺-N pretreatment was conducted. The TAN concentrations before and after FA pretreatment were comparable ($p > 0.05$) (i.e., approximately 800 mg N/L). The SCOD concentration after FA pretreatment was also measured. The secondary sludge solubilization was expressed as the SCOD release divided by the VS of secondary sludge.

Aerobic Digestion Experiments. The aerobic digestion experiments were carried out to evaluate if the secondary sludge degradation could be increased by FA pretreatment during aerobic digestion. Four aerobic digesters (AR1–AR4) were established, with the details shown in Table 1. First, 1.5 L of digesting sludge was added to each digester.

Table 1. Experimental Conditions Employed in the Aerobic Digestion Tests

reactor	experimental conditions
AR1	0.4 L of FA (300 mg N/L) pretreated secondary sludge + 1.5 L of digesting sludge
AR2	0.4 L of untreated secondary sludge + 1.5 L of digesting sludge
AR3	0.4 L of untreated sludge + TAN (170 mg N/L in AR3 at pH 7.0) + 1.5 L of digesting sludge
AR4	0.4 L of supernatant from original secondary sludge + 1.5 L of digesting sludge

For the experimental aerobic digester, 0.4 L of FA pretreated secondary sludge was transferred to AR1, which resulted in the ratio of digesting sludge to secondary sludge being 1.7 based on the dry VS mass. This was to ensure that the amount of digesting sludge was adequate for aerobically digesting secondary sludge. Into AR2 and AR3, which served as the control digesters, was put 0.4 L of secondary sludge without any pretreatment. The ratio of digesting sludge to secondary sludge was also 1.7 in AR2 and AR3 based on the dry VS mass. In addition, an NH₄⁺-N stock solution was also added to AR3, resulting in an additional TAN concentration of 170 mg N/L in AR3. This was to enable the initial TAN concentration in AR3 to be comparable with that (i.e., 800 mg TAN/L \times 0.4 L/1.9 L) in AR1, whereby the impact of TAN on the degradation of secondary sludge in the aerobic digester was assessed. Into AR4 was put 0.4 L of supernatant from original secondary sludge, serving as a blank. During the aerobic digestion experiments, dissolved oxygen (DO) was maintained at >5.0 mg/L. In all aerobic digesters, pH was maintained at 7.0 ± 0.1 during the aerobic digestion. The aerobic digestion experiments lasted for about 15 days. This aligned with the hydraulic retention time (HRT) of the full scale aerobic digester.⁴ Tap water was intermittently added to all the aerobic digesters to compensate for the water that evaporated in the aerobic digestion.

Samples were taken every 2–3 days from each digester during the 15 day period for analyzing TS, VS, and inorganic nitrogen (NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N), which were performed in triplicate. Afterward, the degradation percentage of the secondary sludge and the biomass specific inorganic nitrogen production (i.e., sum of NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N) were calculated as detailed in the section “Calculations and Model Analysis”. All the ammonium/FA was removed in less than 2 days. The dewaterability of aerobically digested sludge (i.e., aerobic digestate) was also assessed by capillary suction time (CST, an indicator of dewaterability) and was expressed as CST divided by the TS content (%) of the digestate (s).

Calculations and Model Analysis. The degradation percentage of the secondary sludge during the aerobic digestion period was determined from the VS destruction in each digester using the following equation:¹⁷

$$P(t_d) = (VS(d_0) - VS(d) - (VS(d_0)_{sup} - VS(d)_{sup})) \times V_R / V_{SS} / VS_{SS} \quad (1)$$

where $P(t_d)$ is the degradation percentage of secondary sludge (%), $VS(d_0)$ is the VS concentration in digesters AR1–AR3 at day 0 (g/L), $VS(d)$ is the VS concentration in digesters AR1–AR3 at day d (g/L), $VS(d_0)_{sup}$ is the VS concentration in AR4 at day 0 (g/L), $VS(d)_{sup}$ is the VS concentration in AR4 at day d (g/L), V_R is the working volume of the digesters (i.e., 1.9 L), V_{SS} is the volume of FA pretreated secondary sludge added to the digester (i.e., 0.4 L), and VS_{SS} is the VS concentration of the secondary sludge (i.e., 7.2 g/L).

The biomass inorganic nitrogen production from secondary sludge was determined based on the inorganic nitrogen concentration (i.e., sum of NH_4^+-N , NO_2^--N and NO_3^--N) using the following equation:¹⁷

$$\text{TIN}(d) = (\text{TIN}(d) - \text{TIN}(d_0) - (\text{TIN}(d)_{sup} - \text{TIN}(d_0)_{sup})) \times V_R / V_{SS} / VS_{SS} \quad (2)$$

where $\text{TIN}(d)$ is the biomass inorganic nitrogen production from secondary sludge (mg N/g VS), $\text{TIN}(d)$ is the inorganic N concentration in digesters AR1–AR3 at day d (mg N/L), $\text{TIN}(d_0)$ is the inorganic N concentration in digesters AR1–AR3 at day 0 (mg N/L), $\text{TIN}(d)_{sup}$ is the inorganic N concentration in digester AR4 at day d (mg N/L), and $\text{TIN}(d_0)_{sup}$ is the inorganic N concentration in digester AR4 at day 0 (mg N/L).

The degradable percentage (Y) and hydrolysis rate (k) are two crucial parameters related to the degradation of secondary sludge in aerobic digestion. They were estimated by fitting the VS-based secondary sludge degradation percentage to a first order kinetic model (eq 3) using Aquasim 2.1d with sum of squared errors (J_{opt}) as an objective function.

$$Y(t) = Y_0(1 - e^{-kt}) \quad (3)$$

where $Y(t)$ is degradation percentage of secondary sludge at time t (%), Y_0 is degradable percentage of secondary sludge (%), k is hydrolysis rate (days^{-1}), and t is time (days). The nondegradable percentage of secondary sludge was calculated as the difference between 100% and Y_0 .

Analysis. Mixed liquor samples from the aerobic digesters were filtered using 0.45 μm pore size disposable Millipore filter unit. Afterward, the inorganic nitrogen concentrations (NH_4^+-N , NO_3^--N and NO_2^--N) of the filtered samples were measured by a Lachat flow injection analyzer. The concentrations of TS and VS were analyzed based on the standard methods.¹⁸ The capillary suction time was measured by a capillary suction timer (case dimension: $22 \times 16 \times 7 \text{ cm}^3$, Triton-WPRL, Type 304). An analysis of variance was used to evaluate the significance of results. Herein, $p > 0.05$ is considered to be statistically insignificant, whereas $p < 0.05$ is considered to be statistically significant.

RESULTS AND DISCUSSION

Impact of FA Pretreatment on Secondary Sludge Solubilisation. The impact of FA pretreatment on secondary sludge solubilisation was evaluated by SCOD release. The SCOD only increased by about $0.04 \pm 0.01 \text{ mg SCOD/mg VS}$ in the control reactors without pH adjustment or ammonium addition. In contrast, SCOD increased by about $0.12 \pm 0.02 \text{ mg SCOD/mg VS}$ after FA pretreatment at $300 \text{ mg NH}_3-\text{N/L}$ for 24 h. This indicates that FA pretreatment could enhance sludge solubilisation.

Impact of FA Pretreatment on Secondary Sludge Degradation in Aerobic Digestion. Full-scale secondary sludge with and without FA pretreatment were added into the aerobic digesters to evaluate their degradability. The degradation of secondary sludge was evaluated based on the VS

destruction and inorganic nitrogen production during aerobic digestion.

The degradation percentage of secondary sludge (VS basis) with and without FA pretreatment over the 15 days aerobic digestion was shown in Figure 1. The secondary sludge was

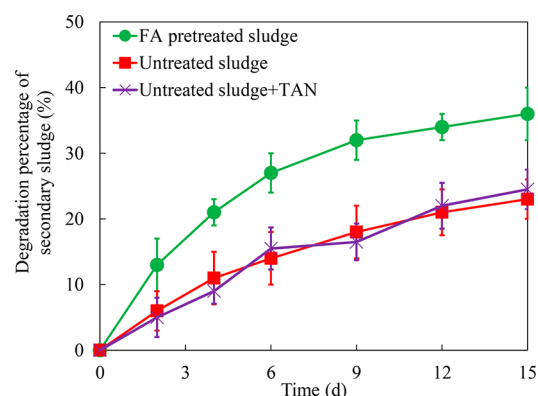


Figure 1. Degradation percentage of secondary sludge (VS basis) with and without FA pretreatment during the 15 days aerobic digestion period.

degraded by $36 \pm 4\%$ in the 15 day aerobic digestion period while being pretreated at $300 \text{ mg NH}_3-\text{N/L}$, whereas only $23 \pm 3\%$ of untreated secondary sludge was degraded in AR2 over the same period. This reveals that secondary sludge degradation in aerobic digestion could be increased by FA pretreatment. It is also interestingly shown in Figure 1 that the improved secondary sludge degradation was mainly achieved in the initial 6 days. Afterward, the degradation of secondary sludge was comparable ($p > 0.05$) for the sludges with and without FA pretreatment. This reveals that the improved secondary sludge degradation could be mainly attributed to the quickly biodegradable part rather than the slowly biodegradable part. This is in agreement with the findings of previous study,¹³ where the quickly biodegradable part was concluded as a major reason for the improved anaerobic sludge degradation.

Figure 2 shows the concentration of biomass inorganic nitrogen production during aerobic digestion. It is obvious that a higher inorganic N production from the FA pretreated secondary sludge was observed in comparison to that without FA pretreatment. The total inorganic N production in the 15

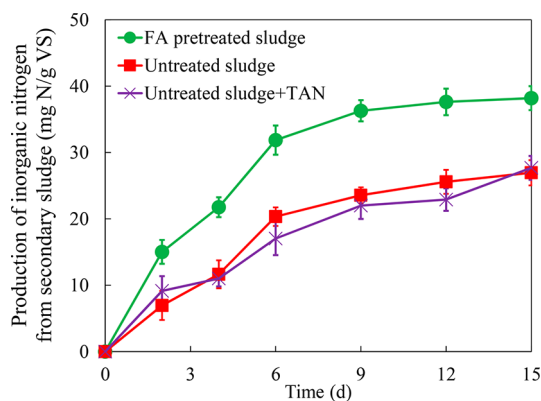


Figure 2. Biomass specific inorganic nitrogen production from secondary sludge with and without FA pretreatment during the 15 days aerobic digestion period.

days aerobic digestion was 38 ± 2 and 27 ± 2 mg N/g VS, respectively, in the cases of secondary sludges with and without FA pretreatment. Since the inorganic N stems from the destruction of the extracellular polymeric substances and/or bacterial cells, the higher inorganic N production suggested a higher secondary sludge degradation. This aligns well with the results of the VS-based secondary sludge degradation. The inorganic N production verified that FA pretreatment is capable of improving secondary sludge degradation in the aerobic digestion.

Degradable Percentage and Hydrolysis Rate of Secondary Sludge. The degradable percentage (Y) and hydrolysis rate (k) of the secondary sludges with and without FA pretreatment were determined by model-based analysis, as summarized in Table 2. FA pretreatment significantly increased

Table 2. Determined Hydrolysis Rate (k) and Degradable Percentage (Y) (VS Basis) of Secondary Sludges with and without FA Pretreatment on the Basis of Model Analysis

parameters	hydrolysis rate (k , days ⁻¹)	degradable percentage (Y , %)		nondegradable percentage (%)
		degraded in aerobic digestion (%)	degradable but not degraded (%)	
untreated sludge	0.12 ± 0.01	23 ± 3	4 ± 3	73 ± 3
FA pretreated sludge	0.21 ± 0.01	36 ± 4	1 ± 4	63 ± 4

($p < 0.05$) k from 0.12 ± 0.01 to 0.21 ± 0.01 days⁻¹, indicating FA pretreatment is effective in enhancing hydrolysis rate of secondary sludge in the aerobic digestion. Similarly, FA pretreatment also substantially increased ($p < 0.05$) Y from 27 ± 3 to $37 \pm 4\%$, indicating FA pretreatment is effective in increasing the degradable percentage of secondary sludge in the aerobic digestion as well. This reveals that FA pretreatment transforms part of the nondegradable materials in the secondary sludge into the degradable ones. The above also suggests that the improved degradation of secondary sludge in the aerobic digestion can be attributed to both the improved hydrolysis rate and the increased degradable percentage of the sludge. In addition, Table 2 also indicates that almost all the degradable materials of the aerobic digestate with FA pretreatment have been degraded in the 15 day aerobic digestion, as indicated by an extremely low degradable percentage of the aerobic digestate (i.e., $1 \pm 4\%$). In contrast, $4 \pm 3\%$ of the aerobic digestate without pretreatment is until degradable. This suggests that FA pretreatment can achieve an aerobic digestate with a better stability.

Dewaterability of Aerobic Digestate. The dewaterability of aerobic digestate with and without FA pretreatment was evaluated by CST. It was observed that the CST of aerobic digestate decreased ($p > 0.05$) from 38 ± 1 to 34 ± 1 s after implementing FA pretreatment, indicating FA pretreatment before aerobic digestion is effective in improving dewaterability of aerobic digestate.

The sludge contains free water and bound water. Free water is easily removed, whereas bound water is difficult to eliminate. Extracellular polymeric substances (EPS) have been reported to play a crucial role in binding bound water by forming a loose but highly hydrated capsule around the bacterial cell wall to aid the survival of the bacterial cell.¹⁹ It has also been reported that

the bound water could be transformed into free water after EPS degradation.¹⁹ In addition, cells also contain water and thus water release could also occur following cell destruction. Our recent studies have demonstrated that FA pretreatment on sludge could destruct EPS and cells.¹³ This would result in the loss of water-binding capacity and open bacteria cells with cell water freed.²⁰ Consequently, the dewaterability of aerobic digestate can be improved. However, it should be noted that the aerobic digestion tests in this study were in a batch mode, which only aimed to demonstrate the feasibility of the proposed FA pretreatment approach. Therefore, continuous tests still need to be conducted in the future to better evaluate the effect of FA pretreatment on the dewaterability of the aerobic digestate. Laboratory centrifuge test or belt filter test instead of CST test should also be used in the continuous tests to quantitatively determine the dry solids content of the dewatered digestate, thereby quantitatively evaluating the improvement of the digestate dewaterability caused by FA pretreatment.

Potential FA Pretreatment Approach for Improving Secondary Sludge Degradation During Aerobic Digestion. In this study, it was demonstrated that FA pretreatment before aerobic digestion of secondary sludge can be used to improve degradation of full-scale secondary sludge for the first time. This was tested experimentally by laboratory aerobic digestion experiments. Model-based analysis further revealed that the improved degradation could be attributed to both the enhanced hydrolysis rate and the increased degradable percentage of secondary sludge.

The proposed FA pretreatment approach is demonstrated in Figure 3. The secondary sludge produced in the wastewater

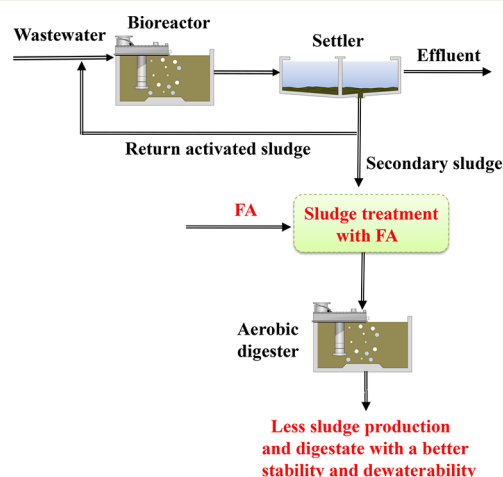


Figure 3. Conceptual graph of the FA pretreatment approach for improving degradation of secondary sludge and achieving an aerobic digestate with a better stability and dewaterability.

treatment process is first fed to the FA pretreatment reactor. The FA pretreated secondary sludge is then fed to the aerobic digester, in which the FA concentration is significantly diluted by >2 orders of magnitude by the digesting sludge in the aerobic digester; thus, the biological activity in the aerobic digester would not be negatively affected. In the aerobic digester, the enhanced sludge degradation can be achieved. The aerobic digestate with FA pretreatment also has a better stability and dewaterability. Therefore, the sludge transport and disposal cost will be substantially reduced. The digestate will be

Table 3. Economic Evaluation of FA Pretreatment Approach for Improving Degradation of Secondary Sludge

	parameters	values
	WWTP size (m ³ /day)	20000
	decay rate of the nitrifiers (days ⁻¹)	0.1 ²²
	decay rate of the heterotrophs (days ⁻¹)	0.2 ²²
	yield of the nitrifiers (g COD/g N) ^a	0.24 ²²
	yield of the heterotrophs (g COD/g COD)	0.625 ²²
	inert COD produced in bacteria decay (g COD/g COD)	0.2 ²²
	mixed liquor suspended solids concentration in the bioreactor (mg/L)	4000
	mixed liquor volatile suspended solids concentration in the bioreactor (mg/L)	3200
	sludge retention time in the bioreactor of the WWTP (days)	10
	mixing energy of the reactor (kwh/(m ³ .days))	0.12
	power price (\$/kwh)	0.1
	solids content in thickened secondary sludge	6%
	solids content in dewatered secondary sludge	15%
	cost of sludge transport and disposal (\$/wet tonne)	30–150 ^{4,23}
	price of NaOH (\$/tonne)	200 ^b
	price of NH ₄ Cl (\$/tonne)	110 ^b
	lifetime of the reactor (year)	20
	interest for initial capital expenditure	8.5%
	secondary sludge degradation (VS basis)	23%
	HRT of the aerobic digester (days)	15
aerobic digester without FA pretreatment	capital cost of aerobic digester (\$)	215000
	annual cost of aerobic digester (\$/year)	23000
	energy cost for oxygen consumption (\$/year)	11000
	sludge transport and disposal cost (\$/year)	75000–380000
	secondary sludge degradation (VS basis)	36%
	HRT of the aerobic digester (days)	15
	capital cost of aerobic digester (\$)	215000
	annual cost of aerobic digester (\$/year)	23000
	secondary sludge pretreatment time by FA (h)	24
	pH in the FA pretreatment reactor	9.0
	TAN concentration in FA pretreatment reactor (mg N/L)	800
aerobic digester with FA pretreatment (assuming same HRT as the aerobic digester without FA pretreatment)	FA concentration in the FA pretreatment reactor (mg N/L)	300
	cost of pH adjustment (\$/year)	500
	cost of TAN (\$/year)	2500
	cost of FA generation (\$/year)	3000
	cost for FA technology implementation (including FA generation cost, FA pretreatment reactor cost, etc.) (\$/year)	6000
	energy cost for oxygen consumption (\$/year)	19000 ^c
	sludge transport and disposal cost (\$/year)	65000–330000
	saving (\$/year)	–4000–36000 ^{d,e}
	secondary sludge degradation (VS basis)	23%
	HRT of the aerobic digester (days)	5
	capital cost of the aerobic digester (\$)	97000
	annual cost of aerobic digester (\$/year)	10000
	secondary sludge pretreatment time by FA (h)	24
	pH in the FA pretreatment reactor	9.0
	TAN concentration in FA pretreatment reactor (mg N/L)	800
aerobic digester with FA pretreatment (assuming same sludge degradation as the aerobic digester without FA pretreatment)	FA concentration in the FA pretreatment reactor (mg N/L)	300
	cost of pH adjustment (\$/year)	500
	cost of TAN (\$/year)	2500
	cost of FA generation (\$/year)	3000
	cost for FA technology implementation (including FA generation cost, FA pretreatment reactor cost, etc.) (\$/year)	6000
	energy cost for oxygen consumption (\$/year)	11000 ^c
	sludge transport and disposal cost (\$/year)	75000–380000
	saving (\$/year)	7000 ^e

^aCOD: chemical oxygen demand. ^bMarket price from <http://www.alibaba.com/>. ^cOxygen consumption was determined according to organic carbon and nitrogen balance.²² ^dThe implementation of FA pretreatment is economically favorable only in cases where the sludge transport and disposal cost is higher than \$40/wet tone. ^eSaving related to the improved dewaterability of aerobic digestate was not included in the economic analysis because the CST test employed in this study did not allow quantitative assessment of the digestate dewaterability. Therefore, the saving would be higher if the improved digestate dewaterability was considered.

dewatered. The liquor will be returned to the head of the WWTP, where the nitrogen in the liquor will be removed via nitrification and denitrification. The dewatered sludge will be transported and disposed. Also, FA is a renewable chemical that can be gained in situ from the reject water of the WWTP, which contains FA at 30–560 mg N/L.^{13,21} Therefore, this FA approach is environmentally friendly. This FA pretreatment approach can also potentially be used to enhance the sludge degradation in the commonly used autothermal thermophilic aerobic digestion, postaerobic digestion (i.e., anaerobic digestion followed by aerobic digestion), and postanaerobic digestion (i.e., anaerobic digestion followed by another anaerobic digestion). This will be further assessed in the future.

A desktop scaling up evaluation on a WWTP of 20 000 m³/d was performed to shed light on the economic potential of the FA pretreatment approach. Two kinds of economic assessment were conducted. One was performed by assuming an identical aerobic digestion time (i.e., HRT) in the two aerobic digesters with and without FA pretreatment. Consequently, the degradation percentages of secondary sludge would be different in these two aerobic digesters, thereby leading to the differences in the oxygen consumption and sludge disposal costs. The other was conducted by assuming an identical degradation percentage of secondary sludge in the aerobic digesters with and without FA pretreatment. Consequently, the aerobic digestion time in these two aerobic digesters would be different, thereby resulting in different volumes and capital costs of the two aerobic digesters.

In the first economic assessment, 15 days of HRT was assumed for the two aerobic digesters with and without FA pretreatment. The aerobic digester with 23% (VS basis) secondary sludge degradation served as a control. The other digester includes FA pretreatment at 300 mg N/L for 24 h, gaining a 36% (VS basis) secondary sludge degradation. The economic assessment results are shown in Table 3. After implementing FA pretreatment, the cost saving is predicted to be −\$4000–36 000/year depending on sludge transport and disposal costs. The FA pretreatment approach would be economically favorable when the sludge transport and disposal cost is higher than \$40/wet tone. The cost saving is from the reduced sludge transport and disposal cost (\$10 000–50 000/year) subtracting the extra cost for oxygen consumption (\$8000/year) and FA pretreatment implementation (\$6000/year, including \$3000/year for FA generation). In the second economic assessment, 6 days of HRT was assumed in the aerobic digester with FA pretreatment, which attained a similar secondary sludge degradation to the aerobic digester with an HRT of 15 days and without FA pretreatment. Table 3 shows that the cost saving is predicted to be \$7000/year. The cost saving stems from the reduced capital cost of the aerobic digester (\$13 000/year) deducting the extra cost for implementing FA pretreatment (\$6000/year, including \$3000/year for FA generation). Therefore, the FA pretreatment approach is economically favorable for improving degradation of secondary sludge in aerobic digestion. In addition, the savings related to the improved dewaterability of aerobic digestate was not included in the economic evaluation because the CST test employed in this study did not allow quantitative assessment of the digestate dewaterability. Therefore, the savings would be higher if the improved digestate dewaterability was considered. Nevertheless, it would be difficult to make the direct quantitative comparison with the other available approaches in terms of cost (e.g., chemical and/or energy

consumption cost) because the result would depend on plenty of factors such as the sludge characteristics. The comparison should be conducted by performing experiments using the same sludge and with the same sludge degradation achieved. However, the FA approach at least shows the advantage qualitatively because it is economically favorable.

This FA pretreatment approach is only in its infancy stage. Consequently, more work needs to be done to comprehensively investigate and optimize this pretreatment approach (i.e., optimizing FA/pH/TAN concentration and pretreatment time). In terms of mechanisms, this study shows that FA pretreatment enhanced the sludge solubilization. Also, model analysis reveals that FA pretreatment improved both degradable percentage and hydrolysis rate of secondary sludge. These could collectively contribute to the enhanced sludge degradation. However, more studies (e.g., chemical structure analysis of sludge/EPS) are still required to explore the mechanisms in more detail. Nevertheless, the scope of the optimization and mechanism exploration would be quite large and therefore would need a comprehensive study that cannot be accommodated in this initial proof-of-concept study.

CONCLUSIONS

Laboratory aerobic digestion tests were conducted in this study to assess the feasibility of improving secondary sludge degradation by FA pretreatment in aerobic digestion. The key conclusions of this study are as follows: (1) Secondary sludge degradation could be enhanced by FA pretreatment prior to aerobic digestion. (2) Both hydrolysis rate and degradable percentage of secondary sludge in aerobic digestion could be increased by FA pretreatment. (3) FA pretreatment can achieve an aerobic digestate with a better stability and dewaterability. (4) The FA pretreatment approach would be economically favorable when the sludge transport and disposal cost is higher than \$40/wet tonne.

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Notes

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REFERENCES

(1) Canales, A.; Pareilleux, A.; Rols, J. L.; Huyard, A. Decreased sludge production strategy for domestic wastewater treatment. *Water Sci. Technol.* 1994, 30 (8), 97–106.

- (2) Wang, Q.; Wei, W.; Gong, Y.; Yu, Q.; Li, Q.; Sun, J.; Yuan, Z. Technologies for reducing sludge production in wastewater treatment plants: State of the art. *Sci. Total Environ.* **2017**, *587-588*, 510–521.
- (3) Song, K.; Zhou, X.; Liu, Y.; Xie, G.-J.; Wang, D.; Zhang, T.; Liu, C.; Liu, P.; Zhou, B.; Wang, Q. Improving dewaterability of anaerobically digested sludge by combination of persulfate and zero valent iron. *Chem. Eng. J.* **2016**, *295*, 436–442.
- (4) Foladori, P.; Andreottola, G.; Zigliio, G. *Sludge Reduction Technologies in Wastewater Treatment Plants*; IWA Publishing: London, 2010.
- (5) Song, L.-J.; Zhu, N.-W.; Yuan, H.-P.; Hong, Y.; Ding, J. Enhancement of waste activated sludge aerobic digestion by electrochemical pre-treatment. *Water Res.* **2010**, *44* (15), 4371–4378.
- (6) Bougrier, C.; Albasi, C.; Delgenès, J.-P.; Carrère, H. Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. *Chem. Eng. Process.* **2006**, *45* (8), 711–718.
- (7) Nah, I. W.; Kang, Y. W.; Hwang, K.-Y.; Song, W.-K. Mechanical pretreatment of waste activated sludge for anaerobic digestion process. *Water Res.* **2000**, *34* (8), 2362–2368.
- (8) Bougrier, C.; Delgenes, J.; Carrere, H. Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge. *Biochem. Eng. J.* **2007**, *34* (1), 20–27.
- (9) Kim, J.; Park, C.; Kim, T.-H.; Lee, M.; Kim, S.; Kim, S.-W.; Lee, J. Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. *J. Biosci. Bioeng.* **2003**, *95* (3), 271–275.
- (10) Cai, W.; Liu, W.; Yang, C.; Wang, L.; Liang, B.; Thangavel, S.; Guo, Z.; Wang, A. Biocathodic methanogenic community in an integrated anaerobic digestion and microbial electrolysis system for enhancement of methane production from waste sludge. *ACS Sustainable Chem. Eng.* **2016**, *4* (9), 4913–4921.
- (11) Merrylin, J.; Kaliappan, S.; Kumar, S.-A.; Yeom, I.-T.; Banu, J.-R. Enhancing aerobic digestion potential of municipal waste-activated sludge through removal of extracellular polymeric substance. *Environ. Sci. Pollut. Res.* **2014**, *21* (2), 1112–1123.
- (12) Ding, W.; Li, D.; Zeng, X.; Long, T. Enhancing excess sludge aerobic digestion with low intensity ultrasound. *J. Cent. South Univ. Technol.* **2006**, *13*, 408–411.
- (13) Wei, W.; Zhou, X.; Wang, D.; Sun, J.; Wang, Q. Free ammonia pre-treatment of secondary sludge significantly increases anaerobic methane production. *Water Res.* **2017**, *118*, 12–19.
- (14) Wei, W.; Zhou, X.; Xie, G. J.; Duan, H.; Wang, Q. A novel free ammonia based pretreatment technology to enhance anaerobic methane production from primary sludge. *Biotechnol. Bioeng.* **2017**, *114* (10), 2245–2252.
- (15) Wang, Q.; Duan, H.; Wei, W.; Ni, B.-J.; Laloo, A.; Yuan, Z. Achieving stable mainstream nitrogen removal via the nitrite pathway by sludge treatment using free ammonia. *Environ. Sci. Technol.* **2017**, *51* (17), 9800–9807.
- (16) Anthonisen, A.; Loehr, R.; Prakasam, T.; Srinath, E. Inhibition of nitrification by ammonia and nitrous acid. *J. Water Pollut. Control Fed.* **1976**, *48*, 835–852.
- (17) Pijuan, M.; Wang, Q.; Ye, L.; Yuan, Z. Improving secondary sludge biodegradability using free nitrous acid treatment. *Bioresour. Technol.* **2012**, *116*, 92–98.
- (18) *Standard Methods for the Examination of Water and Wastewater*; American Public Health Association: Washington, DC, 2005.
- (19) Zhang, H.; Yang, J.; Yu, W.; Luo, S.; Peng, L.; Shen, X.; Shi, Y.; Zhang, S.; Song, J.; Ye, N.; et al. Mechanism of red mud combined with Fenton's reagent in sewage sludge conditioning. *Water Res.* **2014**, *59*, 239–247.
- (20) Chen, Y.; Yang, H.; Gu, G. Effect of acid and surfactant treatment on activated sludge dewatering and settling. *Water Res.* **2001**, *35* (11), 2615–2620.
- (21) Wang, Q. A roadmap for achieving energy-positive sewage treatment based on sludge treatment using free ammonia. *ACS Sustainable Chem. Eng.* **2017**, DOI: [10.1021/acssuschemeng.7b02605](https://doi.org/10.1021/acssuschemeng.7b02605).
- (22) Metcalf and Eddy, AECOM. *Wastewater Engineering: Treatment and Reuse*; McGraw-Hill Inc.: New York, 2003.
- (23) Batstone, D.; Jensen, P.; Ge, H. Biochemical treatment of biosolids—Emerging technologies: Pre-treatment methods such as biological processes can improve performance economically. *Water* **2011**, *38* (3), 90–93.