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Enhanced Deep Utilization of Low-Organic Content Sludge by Processing Time-Extended Low-Temperature Thermal Pretreatment

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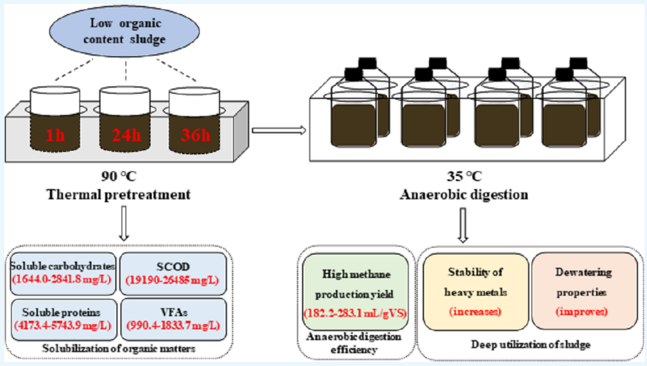
ABSTRACT: Anaerobic digestion is an important way for maintaining sewage sludge stability, reduction, and resource recovery. However, the low organic content generally limits methane production. Recently, thermal hydrolysis has been widely used for sludge pretreatment to improve the anaerobic digestion efficiency. Generally, an increased temperature is preferred to enhance the solubility of organic matters in the sludge. However, high energy requirement comes with increased temperature. Application of low-temperature thermal treatment could overcome this drawback. However, the appropriate low-temperature pretreatment time is still uncertain. In this study, an extended contact time with low thermal pretreatment (90 °C) was chosen to realize a more efficient and economical digestion process of low-organic content sludge. The results demonstrated that the solubilization of proteins and carbohydrates was significantly promoted by the contact time-extended thermal hydrolysis pretreatment. The following anaerobic digestion efficiency of low-organic content sludge was also dramatically improved with the prolonged contact time. The maximum methane production could reach around 294.73 mL/gVS after 36 h of 90 °C treatment, which was 5.56 times that of the untreated groups. Additionally, based on the energy balance calculation, extending the thermal hydrolysis time resulted in a more economically feasible anaerobic digestion than increasing the temperature. The dewatering properties and the stability of the heavy metals were also reinforced, implying the advanced deep utilization of the digested low-organic content sludge. In conclusion, sludge pretreated by low-temperature thermal hydrolysis with a prolonged contact time could be more effective for low-organic content sludge treatment and disposal.



1. INTRODUCTION

Biological treatments, including the traditional activated sludge method, A/O, A^2/O, and SBR, have been widely applied in sewage treatment because of low cost and high efficiency.[1] However, the disposal of the sludges produced by the aforementioned technologies has imposed big economic pressure on the operation of sewage treatment plants.[2] Sewage sludge generally has poor compressibility and dewatering performance, which require considerable energy and resource consumption. Moreover, it may contain toxic and harmful substances such as organic matters, heavy metals, and so forth, which increase the difficulty of sludge treatment and disposal.[3,4] However, the rich organic content could enable the sewage sludge to be used as a soil amendment addition or organic fertilizer after appropriate treatment.[5] Therefore, resource utilization has become a hot and key research issue in the treatment and disposal of sewage sludge.

Anaerobic digestion is one of the primary processes for resource utilization and reduction of sewage sludge.[6] It can reduce the amount of sludge, while producing biogas as a renewable energy source. However, anaerobic digestion usually requires a long start-up time due to the limitation of the biochemically available organic matter content in the inoculated sludge. Accordingly, proper pretreatment is required to make a better bioavailability, methane production, and mass reduction.[7] Processes involving thermal, physical, chemical, biological, (such as ultrasonic, alkali, acid, etc.), or a combination of the above-mentioned multiple treatments have been predominately applied in sewage sludge pretreatments.[8−11] Among all, thermal hydrolysis is a prevalent physicochemical pretreatment for sludge. During thermal hydrolysis, the bacterial cells can be destroyed, releasing the intracellular contents, and the macromolecular substances will be decomposed into small molecules that are easily degraded, such as amino acids, volatile fatty acids (VFAs), and carbohydrates.[4,9,12,13] Sludges that are pretreated by thermal hydrolysis generally could yield higher biogas production during anaerobic digestion. For instance, Xue et al.[13] pointed

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that after 24 h low-temperature thermal hydrolysis or 180 min high-temperature thermal hydrolysis, the SCOD values of the sludge both could reach around 50,000−70,000 mg/L, which consequently accelerated the production of methane in subsequent anaerobic digestion.

However, most of the previous studies preferred to increase the temperature of thermal hydrolysis pretreatment to achieve better efficiency,[4,14−16] which requires a high energy input and largely reduces the overall profit ability of the process.[17] A recent study revealed that a high methane yield was obtained from the sludge treated hydrothermally at 150−190 °C, with the yield increasing by 18−31% compared with that of the control group. However, all the net energy gain from these groups were negative and lower than that from the control group due to the additional energy consumption by hydrothermal treatment.[18] It was reported that lowering the thermal pretreatment temperature might reduce the requirement of energy input so as the total cost. Biswal et al.[12] pointed out that anaerobic digestion with waste active sludge pretreated at 80 °C (0.5−3 h) could be economically feasible, with a net saving cost of 29 dollars. Furthermore, the processing time seems to be more important than temperature when pretreated at a relatively low temperature.[19] Ruffino et al.[20] reported that when pretreated at 70 °C for 15 h, the decomposition rate of the sludge could be increased by 10% compared with 1 h. They also revealed that the extra thermal energy was equal to about 950−3000 MJ/h for the sludge treated at 70−90 °C (3 h) and the process could be self-sustainable. However, little data is available that demonstrated the conduct energy consumption caused by the prolonged pretreatment time. Moreover, in addition to the resource utilization of sludge, effective reduction in the volume of sludge and harmlessness (eliminating or lowering eco-toxicity) of sludge are other two basic requirements for sludge treatment and disposal.[1,21] It is not clear whether the pretreatment for extended time combined with anaerobic digestion can effectively improve the dewatering properties and heavy metal stability of the sludge.

Herein, in this study, we aimed to reduce the cost and improve the performance of anaerobic digestion of low-organic matter content sludge by prolonging the pretreatment time under the condition of low thermal hydrolysis (90 °C). Furthermore, the effects on the dewatering performance and stability of heavy metals of the treated sludge were also investigated. The results could provide scientific reference for resource utilization, harmlessness, and reduction of low organic sludge in actual engineering projects.

2. MATERIALS AND METHODS

2.1. Raw and Seed Sludge. The raw sludge for the thermal hydrolysis pretreatment was composed of excess activated sludge and dewatered sludge, with a moisture content of 90%. The excess activated sludge was collected from the sludge concentration tank of a waste water treatment plant in Fuzhou, China, while the dewatered sludge was collected from the subsequent dehydrating unit. All these sludges were stored at 4 °C but used up within 2 weeks. Seed sludge for anaerobic digestion was taken from an ovoid anaerobic digester of a waste water treatment plant at Shanghai, China. The characteristics of the raw and seed sludge are listed in Table 1.

Table 1. Basic Properties of Raw and Seed Sludge at 25 °C

parameters	unit	raw sludge	seed sludge
pH		6.9	7.3
total solids (TS)	%	9.7	9.0
volatile solids (VS)	% TS	54.8	44.9
total chemical oxygen demand (TCOD)	mg/L	79993.3	65423.6

2.2. Low-Temperature Thermal Hydrolysis Pretreatment. Raw sludge, in which the moisture content was 90%, was placed in a water bath at 90 °C for 1, 24, and 36 h, respectively. After the thermal treatment, the feed was cooled down to room temperature and stored in the refrigerator for the following anaerobic digestion, dewaterability, and heavy metals tests. Meanwhile, SCOD, carbohydrates, proteins, and VFAs of the raw and pretreated sludge samples were analyzed.

2.3. Anaerobic Digestion. *2.3.1. Anaerobic Digestion System.* The sludge pretreated at different times (90 °C 1, 24, and 36 h, respectively) was separately mixed with the seed sludge at a ratio of 1:2 VS (mass). Then, 160 g of the mixture was added into bottles (250 mL) for batch-scale anaerobic digestion experiments. The unpretreated raw sludge was mixed with seed sludge in the same ratio to be used as the control group. After the mixture was added, the bottles were flushed with N_2 for 3 min to remove O_2. The biogas production was determined from the displacement of the saturated sodium chloride solution using the drainage method. The batch anaerobic digestion experiments were conducted in a water bath at a constant temperature of 35 °C.

2.3.2. Modeling of Methane Production. The modified Gompertz equation was used for nonlinear fitting of methane production[22,23] in this study, and the equation is as follows

$$B = P \cdot \exp(-\exp(R_m \cdot e(\lambda - t)/P) + 1) \quad (1)$$

where B represents methane production, mL/gVS; P is the maximum methane production, mL/gVS; R_m is the maximum methane yield rate, mL/gVS·d; λ is the lag time, d; and t represents the reaction time, d.

The parameters P, R_m, and λ were analyzed using the nonlinear regression approach by Origin 2017.

2.4. Extraction of Heavy Metals. The concentrations of heavy metals (Cu, Zn, Pb, Cd, Cr, and Ni) of the raw sludge, pretreated sludge, and anaerobic digestion sludge were extracted. The sequential extraction procedure proposed by Tessier et al.[24] was used to determine the chemical speciation of heavy metals. Heavy metals in sludge can be divided into five existing forms: exchangeable (F1), bound to carbonates (F2), bound to Fe and Mn oxides (F3), bound to organic matter (F4), and residual (F5). The detailed extraction process for each form is described below

F1 (exchangeable): 2 g of the sludge samples and 16 mL of $MgCl_2$ were added to a 50 mL plastic centrifuge tube and shaken for 2 h at room temperature.

F2 (bound to carbonates): 16 mL of 1 mol/L $C_2H_3O_2Na$ was added to the residues from F1, adjusting to pH 5 with $C_2H_2O_4$, followed by shaking for 2 h at room temperature.

F3 (bound to Fe and Mn oxides): the residues from F2 were shaken at 96 °C in a water bath for 2 h with 40 mL of 0.04 mol/L $NH_2OH \cdot HCl$.

F4 (bound to organic matter): 10 mL of 30% H_2O_2 and 6 mL of 0.02 mol/L HNO_3 were added to the residues from F3, adjusting to pH 2 with HNO_3; the mixture was then shaken for 2 h at 85 °C in a water bath. Subsequently, a second addition of 5 mL of 30% H_2O_2 (adjusted to pH 2 with nitric acid) was added, and the mixture was shaken again at 85 °C in a water

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bath for 1.5 h. 10 mL of 3.2 mol/L $C_2H_3O_2NH_4$ was added to the residues and then shaken for 0.5 h.

F5 (residual): the residues of F4 were dissolved in mixed acid (HNO_3, $HClO_4$, and HF).

The concentrations of Cu, Zn, Pb, Cd, Cr, and Ni in different fractions were determined by inductively coupled plasma optical emission spectrometry (ICP).

2.5. Evaluation of the Risk Assessment Code. The risk assessment code (RAC) is widely used for environmental risk assessment of heavy metal pollution in the soil and sediments.[25] The RAC values show the availability of metals by applying a scale to the percentage of metals present in F1 + F2, as expressed in eq 2

$$\mathrm{RAC} = C_{(\mathrm{F1+F2})}/C_{\mathrm{n}} \times 100\% \tag{2}$$

where C_n is the total content of heavy metals in the sample. The classification of risk according to the RAC is as follows: no risk (NR), RAC ≤ 1%; low risk (LR), 1% ≤ RAC ≤ 10%; medium risk (MR), 11% ≤ RAC ≤ 30%; high risk (HR), 31% ≤ RAC ≤ 50%; and very high risk, RAC > 50%.

2.6. EPS Extraction and Determination. Two EPS fractions, loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS), were separately extracted from the studied sludge according to the method modified by Li et al.[26−28] First, 50 mL of sludge was centrifuged for 5 min at 4000 rpm. The supernatant was discarded. The sludge mixture was then diluted to 50 mL with 0.05% NaCl solution (preheated to 70 °C). Afterward, the sludge suspension was sheared using a multiple oscillator for 5 min, followed by centrifugation for 10 min at 4000 rpm. The organic matter in the supernatant was considered as LB-EPS in this study. Next, the sludge pellets left in the centrifuge tube were diluted to 50 mL again with 0.05% NaCl solution (preheated to 70 °C). The sludge suspension was then heated in a water bath at 60 °C for 30 min; afterward, the sludge mixture was centrifuged for 15 min at 4000 rpm. The collected supernatant was regarded as TB-EPS. Proteins (PN), polysaccharides (PS), and nucleic acids (NA) in the extracted LB-EPS and TB-EPS were determined.

2.7. Energy Balance Model in the Thermal Hydrolysis Pretreatment Anaerobic Digestion. Theoretical calculation of energy balance was performed based on the experimental data. The input energy (Q_{input}) was calculated referring to eqs 3 and 4.[29] In this study, the Q_{input} with pretreatment could be calculated according to eq 5, considering the much longer pretreatment time.

$$Q_{\mathrm{input}} = \rho VC(T_{\mathrm{d}} - T_{\mathrm{a}}) + 0.0864\, kA\tau_{\mathrm{e,AD}}(T_{\mathrm{d}} - T_{\mathrm{a}}) \tag{3}$$

$$Q_{\mathrm{input}} = \rho VC(T_{\mathrm{th}} - T_{\mathrm{a}}) - \xi\rho VC(T_{\mathrm{th}} - T_{\mathrm{d}}) + 0.0864\, kA\tau_{\mathrm{e,AD}}(T_{\mathrm{d}} - T_{\mathrm{a}}) \tag{4}$$

$$Q_{\mathrm{input}} = \rho VC(T_{\mathrm{th}} - T_{\mathrm{a}}) - \xi\rho VC(T_{\mathrm{th}} - T_{\mathrm{d}}) + 0.0864\, kA\tau_{\mathrm{e,AD}}(T_{\mathrm{d}} - T_{\mathrm{a}}) + 0.0864\, kAt_{\mathrm{th}}(T_{\mathrm{th}} - T_{\mathrm{a}}) \tag{5}$$

where Q_{input} is the input energy, MJ/t; ρ is the density of sludge, kg/m^3; V is the volume of sludge, m^3; C is the specific heat of sludge, MJ/kg °C; T_{th} is the thermal hydrolysis pretreatment temperature, °C; T_a is the ambient temperature, °C; T_d is the anaerobic digestion temperature, °C; ξ is the energy recovery efficiency, %; k is the heat transfer coefficient, W/m^2 °C; A is the surface area of the reactor wall, considering a 2:1 diameter to height ratio, m^2; $\tau_{e,AD}$ is the effective methane production duration for anaerobic digestion, d (Table S2); and t_{th} is the thermal hydrolysis pretreatment time, *d*. The coefficient 0.864 was used for unit conversion from W to MJ/d. In this study, values of the above parameters can be found in Table S1.

The output energy (Q_{output}) was calculated according to eq 6.

$$Q_{\mathrm{output}} = q \times V_{\mathrm{CH_4}} \times \eta \tag{6}$$

where Q_{output} is the output energy, MJ/t; q is the lower heating value of methane, MJ/m^3; V_{CH_4} is the methane yield produced from 1 m^3 sludge of each experimental group; and η is the energy conversion efficiency, %. The values of q and η are summarized in Table S1.

Ultimately, the net energy balance (ΔQ) was calculated using the following equation

$$\Delta Q = Q_{\mathrm{output}} - Q_{\mathrm{input}} \tag{7}$$

2.8. Analytical Methods. TS and VS analyses were performed using standard methods.[30] COD and SCOD were measured using a model 5B3C COD meter. A model PHS-3C pH meter was used to determine the pH. Soluble proteins were quantified using a modified Lowry method with bovine serum albumin as the standard. The phenol sulfuric method with glucose as a standard was used to determine soluble carbohydrate concentrations. The VFA concentration in the soluble fraction was measured using a gas chromatograph. The biogas volume was measured using the draining saturated saltwater method, and the biogas composition was measured by gas chromatography separation. Sludge dewaterability was evaluated in terms of the water content (W_C) in dewatered sludge.[31] A differential scanning calorimeter was used to measure the bound water content.[32] The CST measurement was conducted using the OFITE capillary suction time equipment. The PN, PS, and NA of the extracted EPS were measured according to the Coomassie brilliant blue method, Anthrone method, and colorimetric method.

3. RESULTS AND DISCUSSION

3.1. Effects of Thermal Hydrolysis Pretreatment on Anaerobic Digestion Performance. In this study, anaerobic digestion experiments were performed to investigate the changes in sludge biodegradability caused by thermal hydrolysis pretreatment. As shown in Figure 1, the thermal hydrolysis pretreatment time had significant influence on cumulative methane production. The maximum methane production of the sludge treated at 90 °C for 1 h (182.2 mL/gVS) was about 3 folds of that of the untreated groups (53.05 mL/gVS) and could increase to 5 folds after being treated for 36 h (283.1 mL/gVS). The profiles and the maximum methane production values could reach the same level as that of high-organic content sludges.[14,15,23,33] For instance, in the study by Toutian et al.,[14] the biomethane potential of the thermally hydrolyzed waste active sludge (the VS of the sludge was 73.4% TS) at temperatures of 90−170 °C was around 170.26−301.73 mL/gVS. The results demonstrated that low-temperature thermal hydrolysis is an efficient pretreatment for the anaerobic digestion of sludge with a low organic content. The fitting results of the Gompertz model further supported the above consequence (Table S2), and the estimated maximum methane production could reach 294.73

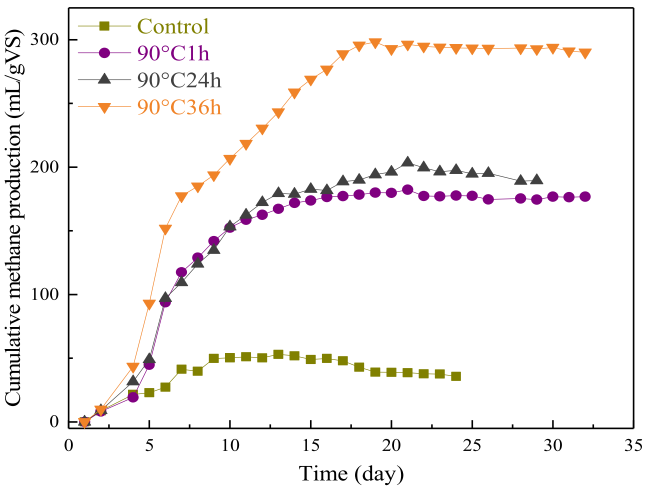

Figure 1. Cumulative methane yield under 35 °C batch anaerobic digestion after thermal pretreatment at 90 °C for 0, 1, 24, and 36 h.

mL/gVS for 36 h of treatment, indicating the superior methane production potential of this low-temperature thermal hydrolysis-anaerobic digestion combined method.

Most of the current studies preferred combining high temperature with short time for anaerobic digestion pretreatment.[4,14,15] For example, in the study by Yang et al.,[15] three dewatered sludges were pretreated at 160 °C for 90 min before anaerobic digestion. However, the methane production potential of the sludge pretreated for a prolonged contact time at a low temperature could be superior to that treated at a high temperature with a short contact time. In the study by Yan et al.,[34] the maximum methane production only reached 144.7 ± 4.4 mL/gVS even when the pretreatment temperature was 120 °C, which is nearly a half of the value in the present study (283.1 mL/gVS). Furthermore, in order to evaluate the economic sustainability of thermal pretreatment, the energy balance was simply calculated under ideal conditions. According to the energy balance calculation, extending the time did not result in a large energy loss and could even show some economic value (Table 2). The net energy balance was calculated to be about 153.37, 153.55, and 281.34 MJ/t, when the pretreatment time was 1 h, 24 h, and 36 h, respectively. Specifically, the input energy of 36 h was 44.83 MJ/t higher than that obtained in 1 h treatment, while the output energy was 172.79 MJ/t higher and the extra energy released was almost 4 times the extra energy consumed. Clearly, extending the pretreatment time at low temperatures markedly reduced the energy consumption and benefited energy release.

Table 2. Energy Balance of Sludge under 35 °C Batch Anaerobic Digestion after Thermal Pretreatment at 90 °C for 0, 1, 24, and 36 h

sample	Q_{output} (MJ/t)	Q_{input} (MJ/t)	ΔQ (MJ/t)
control	90.86	112.06	−21.2
90 °C, 1 h	312.05	158.68	153.37
90 °C, 24 h	348.20	194.65	153.55
90 °C, 36 h	484.85	203.51	281.34

3.2. Effects of Low-Temperature Thermal Hydrolysis Pretreatment on the Physicochemical Properties of Sludge. The release of intracellular soluble organic matters was due to thermal hydrolysis pretreatment, which subsequently facilitated the growth of various bacteria during the anaerobic digestion process.[13] In this study, the physicochemical properties of the pretreated sludge, including the changes in the concentration of soluble organic matters (i.e., soluble carbohydrates and soluble proteins) and the variations in VFA composition, were investigated.

As shown in Figure 2a, the concentration of SCOD increased with the extension of pretreatment time. The SCOD concentration of the untreated group was about 1414.5 mg/L and separately increased to 19,190; 24,905; and 26,485 mg/L after being hydrolyzed for 1, 4, and 36 h, respectively. Specifically, proteins and carbohydrates were proved to be the main constituents of biodegradable organic compounds in the sludges.[34] The concentrations of soluble carbohydrates at 1 h, 24 h, and 36 h were 46, 67, and 79 folds of the raw sludge, respectively. However, the amount of the soluble proteins was 46, 58, and 63 folds of the raw sludge. The promotion of the soluble and degradable component concentration was supposed to provide abundant nutrients for the following methanogen growth and methane production during the digestion process.[35] Interestingly, the solubilization of the low organic content sludge was consistent with those studies which chose high organic content sludge for thermal hydrolysis pretreatment.[4,12,13,17,36] For instance, Biswal et al.[12] reported that when the VS of the sludge was 72.8% TS, the solubilization of SCOD, soluble proteins, and soluble carbohydrates could increase 10, 31, and 36 folds, respectively. The VS was 54.8 %TS for the present study; however, the solubilization of SCOD, soluble proteins, and soluble carbohydrates was 14−19, 46−63, and 46−79 folds of the raw sludge, respectively. It revealed that for low-organic content sludge, prolonging the time of thermal hydrolysis is more helpful for the release of organic matter than increasing the temperature.

VFAs also accumulated as a result of the thermal hydrolysis pretreatment time (Figure 2b). The fermentation of carbohydrates, proteins, and lipids might directly produce acetic, propionic, butyric, and iso-butyric acids,[37] which resulted in the increase of VFA concentration.[38] In present study, the VFAs were mainly composed of acetic, propionic, iso-butyric, and iso-valeric acids. The production rate of acetic acid after 1, 24, and 36 h of treatment at 90 °C was the fastest, and the percentage of acetic acid ranked the top of all the VFAs, over 60% in total. Acetic acid could be readily converted into CH_4 compared to other VFAs,[4] implying that an enhanced methanogenic performance would be caused by thermal hydrolysis pretreatment.

Above all, for low-organic content sludge, prolonging the time of thermal hydrolysis at low temperatures could also facilitate the release of organic matter, which could reach the same level as that of increasing the pretreatment temperature. In general, increasing the temperature actually requires a larger energy input. While the calculated energy balance in Section 3.1 shows that extending the pretreatment time at low temperatures significantly reduced the energy consumption and benefitted energy release. That is, low-temperature hydrolysis with a prolonged contact time is a more economical and efficient pretreatment method.

3.3. Heavy Metal Distribution. The improper disposal of heavy metals may lead to significant environmental impacts such as public health risks, soil, and water pollution.[39] It is widely accepted that the bioavailability and ecotoxicity of heavy metals in the sludge mainly depend on their chemical

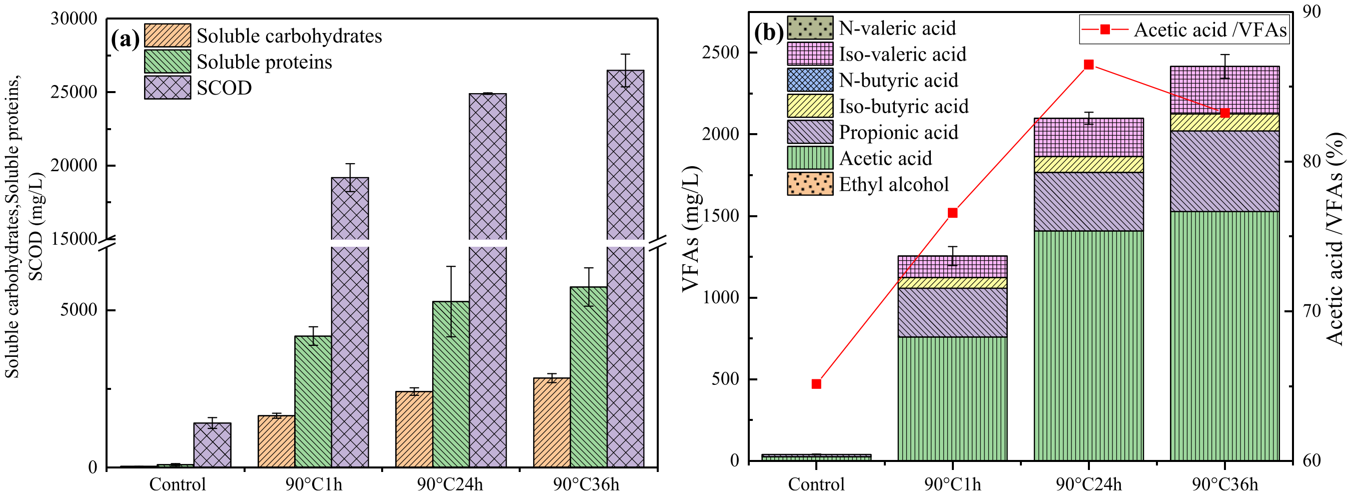

Figure 2. SCOD, soluble carbohydrates, soluble proteins (a), VFA composition, and percentage of acetic acid in VFAs (b) of sludge after thermal pretreatment at 90 °C for 0, 1, 24, and 36 h.

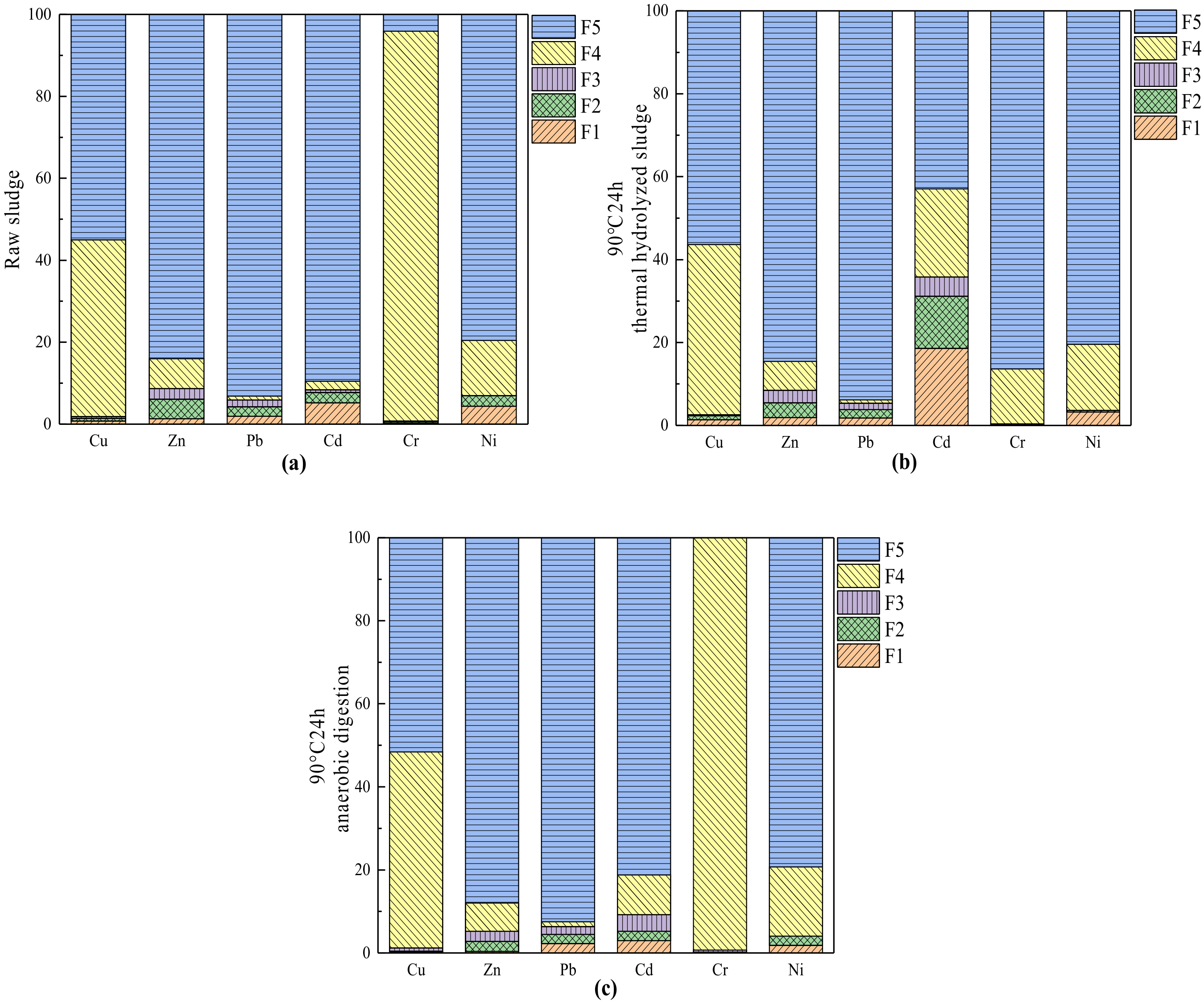

Figure 3. Speciation of heavy metals in raw sludge (a), thermally hydrolyzed (90 °C for 24 h) sludge (b), and anaerobically degraded sludge (35 °C batch anaerobic digestion after 90 °C thermal pretreatment for 24 h) (c).

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Table 3. Environmental Safety Evaluation

sample	heavy metals (F1 + F2)					
	Cu	Zn	Pb	Cd	Cr	Ni
raw sludge	1.44/LR	6.11/LR	4.24/LR	7.71/LR	0.56/NR	6.97/LR
thermal hydrolyzed sludge	2.3/LR	5.47/LR	3.82/LR	31.17/HR	0.29/NR	3.65/LR
anaerobic degraded sludge	0.42/NR	2.81/LR	4.47/LR	5.2/LR	0.19/NR	4.08/LR

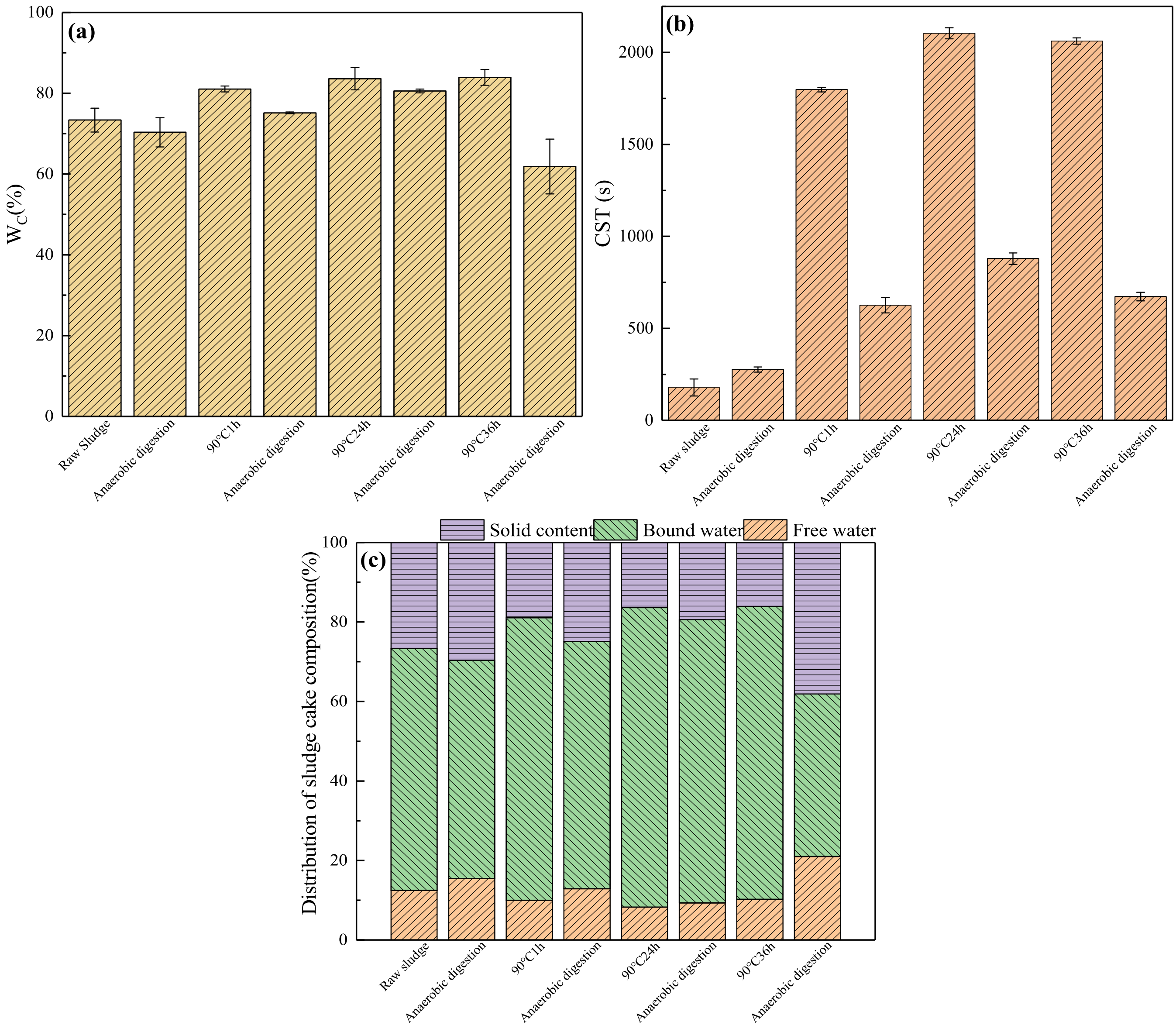

Figure 4. Water content of filter cake (a), CST of sludge (b), and distribution of sludge cake composition (c) under 35 °C batch anaerobic digestion after 90 °C thermal pretreatment for 0, 1, 24, and 36 h.

speciation.[40] Therefore, extraction of heavy metals was performed to investigate whether the heavy metals contained in sludge can be well stabilized after thermal treatments and anaerobic digestion.

Chen et al.[41] established the relationship between heavy metal fractions, eco-toxicity, and bioavailability through the improved BCR sequential extraction. The modified relationship among the fractions of heavy metals, eco-toxicity, and bioavailability[21] is shown in Table S3. Among them, F1, F2, and F3 were readily absorbed by soil, plants, and surface water, presenting a high bioavailability of the associated metals.[42] They were identified as direct effect fractions. F4 was identified as a potential effect fraction because the organic fraction (F4) could be degraded, leading to the release of soluble metals under oxidizing conditions.[43] F5 was identified as a stable fraction. As shown in Figure 3, the speciation of Cu, Zn, Pb, Cr, Cd, and Ni mainly existed in a relatively stable state (F4) and stable state (F5). However, Cd was greatly affected by thermal hydrolysis pretreatment; the speciation of Cd significantly converted from F5 to other fractions, especially F1, F2, and F3, which might bring hazardous effects to the local environments during its migration. Fortunately, the

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Table 4. Contents of Each Component of EPS (mg/L)

sample	PS		PN		NA	
	TB	LB	TB	LB	TB	LB
raw sludge	257.900	92.900	83.314	31.886	90.50	36.50
anaerobic digestion	90.950	60.950	45.720	35.006	47.50	34.00
90 °C, 1 h	620.900	524.900	280.457	208.457	215.00	128.00
anaerobic digestion	68.950	97.950	40.063	51.549	38.50	50.00
90 °C, 24 h	295.900	258.900	161.314	146.314	89.00	90.50
anaerobic digestion	100.950	86.950	36.720	46.577	56.00	46.50
90 °C, 36 h	329.900	279.900	193.457	167.743	89.00	114.50
anaerobic digestion	114.450	128.950	59.434	70.577	57.50	62.00

anaerobic digestion process enhanced the stability of Cd; its potential toxicity and bioavailability were greatly reduced.

The results of the environmental risk assessment based on the RAC showed that all the heavy metals show low or no risks after thermal hydrolysis pretreatment combined with the anaerobic digestion technology (Table 3). The results were mutually verified with the discussion of the bioavailability and ecotoxicity of heavy metals. In summary, thermal hydrolysis pretreatment combined with anaerobic digestion technology can be used as an effective way for sludge treatment and disposal.

3.4. Dewatering Properties. Dewatering is considered to be a bottleneck for sludge treatment; the improvement of dewaterability is essential to reduce the treatment cost.[1] Most studies have reported that improving the sludge dewatering performance by thermal pretreatment required a high temperature of at least 150 °C; 180 °C was the best to improve dewatering.[1,44−46] Therefore, it is necessary to investigate whether the treatment process of thermal hydrolysis and anaerobic digestion in this study would affect the subsequent dewatering performance of the sludge. The W_C of the filter cake, CST, bound water, and EPS of sludge after thermal pretreatment and anaerobic digestion were measured to investigate the effect of thermal pretreatment and anaerobic digestion on sludge dewatering performance.

According to Figure 4a,b, 90 °C thermal hydrolysis pretreatment worsened the dewatering performance of sludge but it was enhanced by subsequent anaerobic digestion. The W_C of the filter cake increased from 73.4 to 81.1, 83.6, and 83.9% when the pretreatment time was 0, 1, 24, and 36 h, respectively, and further decreased to 70.33, 75.12, 80.57, and 61.88% after anaerobic digestion. The change in CST was in accordance with the change in W_C. This indicated that thermal hydrolysis combined with anaerobic digestion was favorable for sludge dewatering. The result is similar or superior to other dewatering technologies such as ultrasonic, mechanical, and chemical treatments.[47−49] For instance, Lu et al.[48] reported that the W_C of cake sludge generated from the Fenton-like process ranged from 82 to 84%, and the Fenton process showed a higher efficiency in the removal of water content, with the W_C of cake sludge being 72−78%.

Bound water is the water that is bound to the sludge or trapped between the sludge particles, which cannot be removed by mechanical methods.[31] It can be seen from Figure 4c that thermal pretreatment at 90 °C could not release bound water but the bound water was converted into free water in subsequent anaerobic digestion, which improved the dewatering performance. EPS plays an important role in the formation of sludge flocs; the main components of EPS are proteins (PN) and carbohydrates (PS).[50] These substances can combine with bacteria cells and water to increase sludge viscosity and deteriorate dewatering performance.[51] It has been documented that the amount of LB-EPS was closely related to sludge flocculation and settle ability, whereas the amount of TB-EPS had no correlation with sludge characteristics.[26] Changes in the two EPS fractions, loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS), during anaerobic digestion are shown in Table 4. In this study, the mass of LB-EPS of PN, PS, and nucleic acid (NA) increased significantly after thermal hydrolysis, trapping the bound water correspondingly and worsening the dewatering properties.[45] On the other hand, during anaerobic digestion, the mass of LB-EPS of PN, PS, and nucleic acid (NA) of thermally hydrolyzed sludge dropped apparently and reached about 53.9−81.3%, which is much greater than 6.8−34.4% of the control group. In conclusion, anaerobic digestion after thermal hydrolysis caused the degradation of the EPS, finally disrupting the complex sludge floc structure and releasing the bound water; therefore, the sludge dewatering performance could be improved.

4. CONCLUSIONS

In this study, processing time-extended low-temperature thermal pretreatment was applied to achieve low energy consumption in the anaerobic digestion of sludge with low organic contents (VS = 54.8% TS). In addition to the resource utilization of sludge, effective reduction in the sludge volume and harmlessness were investigated. The results suggested that prolonging the contact time of thermal hydrolysis was more helpful in promoting the anaerobic digestion efficiency than increasing the hydrolysis temperature. The maximum methane production reached 294.73 mL/gVS after pretreatment at 90 °C for 36 h, which was 5.6 folds the untreated group and around 2 folds of that obtained in the previous reported results. Moreover, the positive energy balance could go up to 281.34 MJ/t when pretreating the sludge at 90 °C for 36 h for anaerobic digestion, implying that thermal hydrolysis pretreatment with an extended contact time was also cost-effective and efficient. Furthermore, processing time-extended low-temperature thermal pretreatment of the low organic content sludge could improve the sludge dewatering capacity and lower the migration and transformation of heavy metals, which might lead to a better deep utilization. In conclusion, the processing time-extended low-temperature thermal pretreatment combined with anaerobic digestion is beneficial to reduce energy consumption and improve the properties of sewage sludge, thereby enhancing the feasibility and greenness of the anaerobic digestion technology in practical engineering applications.

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■ ASSOCIATED CONTENT

Supporting Information

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Energy balance parameters; parameters from Gompertz equation modeling and thermal hydrolysis pretreatment effects; and relation among fraction of heavy metals, stability, eco-toxicity, and bioavailability (PDF)

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Notes

The authors declare no competing financial interest.

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