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Methane production improvement in an osmotic membrane bioreactor for sludge anaerobic digestion: pretreatment optimization and long-term performance

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ABSTRACT

Hydrolysis is the first step and also rate-limiting step of anaerobic digestion which recovers energy from waste sludge. In order to accelerate the reaction rate of the hydrolysis, many pretreatment conditions had been taken into account. In this study, thermal pretreatment and alkaline pretreatment were combined with each other, serving as a thermal-alkaline pretreatment approach. Firstly, an orthogonal designed batch experiment was conducted to evaluate the pretreatment conditions, and then the optimal conditions were applied to an osmotic membrane bioreactor for a long-term investigation. Based on batch experiments, sludge treated by NaOH at pH 9 or 10 showed a better effect in cell solubilization. Sludge treated by $Ca(OH)_2$ at pH 9, and sludge treated by NaOH at pH 9 or 10 showed advantages in methane production. Ultimately, sludge treated by NaOH at pH 9 and then heated at 90 °C for 60 min was selected as the optimal pretreatment condition. During the long-term operation of osmotic membrane bioreactor for sludge anaerobic digestion, the volume methane production of the sludge treated by thermal-alkaline was maintained at around 200–300 mL/L/d, which was 2–3 times of the sludge treated by ultrasound.

Key words: anaerobic digestion, methane, osmotic membrane bioreactor, pretreatment, sewage sludge

HIGHLIGHTS

- Thermal-alkaline pretreatment was optimized according to an orthogonal experimental design.
- Effects of thermal-alkaline pretreatment on the performance of an osmotic MBR for sludge anaerobic digestion were systematically studied.

1. INTRODUCTION

The increasing amount of sewage sludge has raised great concern (Yang *et al.* 2015). For the treatment of excess sewage sludge, efficiency and cost-effectiveness should be considered in the first place. Anaerobic digestion (AD) is an effective process which can realize mass reduction, sludge valorization and resource utilization (through methane production) simultaneously (Zhang *et al.* 2019a). An emerging osmotic membrane bioreactor developed for waste sludge anaerobic digestion (adFO-MBR) showed better performance, e.g., higher organic degradation and methane content in biogas (Zhao *et al.* 2018). The way to achieve a high solid concentration was different in the adFO-MBR in comparison with a conventional AD reactor. The adFO-MBR can achieve the separation of solid retention time and hydraulic retention time simultaneously and raise the solid content in the reactor by drawing the moisture out with forward osmosis. Although the performance of adFO-MBR had already been studied (Zhao *et al.* 2019), there still is a distinct knowledge gap about how to enhance the effect of sludge anaerobic digestion in adFO-MBR. Specifically speaking, the organic loading rate of the adFO-MBR was low, only 1.50 g VS/(L·d), which should be improved to make adFO-MBR more suitable for engineering practice.

The AD process is generally divided into four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is the first stage of the AD process and the well acknowledged rate-limiting stage, during which complex and insoluble organic compounds are decomposed to simple and soluble molecules (Deepanraj *et al.* 2014; Adekunle & Okolie 2015). Pretreatment is an effective way to increase the hydrolysis rate (reflected as an increase in soluble chemical oxygen demand

(SCOD), soluble polysaccharides and soluble proteins), methane potential and biogas production rate (Yang *et al.* 2018; Du *et al.* 2019; Wang *et al.* 2019a).

The pretreatment conditions were normally divided into four categories: mechanical pretreatment, thermal pretreatment, chemical pretreatment and biological pretreatment (Zhen *et al.* 2017). Ultrasonication is a well-developed mechanical pretreatment method. Many researchers have studied the effects of ultrasonic pretreatment approach on sludge anaerobic digestion (Appels *et al.* 2008; Li *et al.* 2017; Roebuck *et al.* 2019). The ultrasonic pretreatment occurred in different energies and different durations, all of which brought about higher organic matter solubilization and biogas production than the sludge untreated. However, the results also differed based on the sludge types used (Li *et al.* 2018; Roebuck *et al.* 2019). Thermal pretreatment is another widely used pretreatment method, which could be conducted at different temperatures and various durations. Choi *et al.* (2018) either fixed the durations or fluctuated both the temperature and reaction time, using the response surface methodology (RSM) to select an optimum condition for thermal pretreatment. In other studies, the thermal pretreatment method was proved to be able to promote the solubilization of volatile solids and the methane production during the AD process (Jeong *et al.* 2019; Zhang *et al.* 2019b). Furthermore, it has been concluded that in thermal pretreatment approach, heating temperature seemed to be more important than heating time in terms of enhancing the effect of anaerobic digestion (Kor-Bicakci & Eskicioglu 2019). Alkali pretreatment is a widely used pretreatment approach in chemical pretreatment. The alkaline treatment method is to dissolve some particulate components in the sludge by adding an alkaline reagent, which causes the sludge cells to rupture and accelerates the utilization of the dissolved substances by microorganisms and hydrolytic enzymes. The effect of alkali treatment on sludge disintegration is related to the type and dosage of alkali. Jin *et al.* (2016) compared the cell solubilization effects of different types of alkaline used for pretreatment and concluded that the effects of them ranked as the following order: $NaOH > KOH > Mg(OH)_2 > Ca(OH)_2$. Generally, the most widely used type of alkaline for pretreatment is NaOH. A latest study found that besides the acceleration of hydrolysis and acidification, the alkali pretreatment also has destructive power to the flocculant polyacrylamide which exhibits toxicity in the anaerobic digestion of sludge (Liu *et al.* 2021). Wang *et al.* (2019b) compared chemical pretreatment to thermal pretreatment and achieved a higher carbon removal rate in chemical pretreatment. In practical applications, alkali pretreatment was often combined with thermal pretreatment, serving as thermal-alkaline pretreatment (Wang *et al.* 2019b). In comparison between thermal-alkaline pretreatment and thermal pretreatment, it was found that the effect of hydrolysis and biogas production of the former were better than that of the latter (Chiappero *et al.* 2019; Chen *et al.* 2020). In addition, researchers also used response surface methodology for the optimization of temperature, reaction time and pH in thermal-alkaline pretreatment and concluded that 75 °C, 17.5 h, pH 11.0 were the desirable thermal-pretreatment conditions (Liu *et al.* 2019). However, when the heating temperature was in low range ($<$100 °C), it probably needs a long heating time. And four factors including the heating temperature, heating time, the type, and amount of alkali added had not been optimized in previous studies. As a result, the selection and optimization of the type of alkali, the amount of alkali, the heating time (relatively short), and heating temperature ($<$100 °C) should be conducted when a thermal-alkaline pretreatment approach is utilized and the optimized result could be used to the operation of the reactor.

The objective of this study is to first select an optimal set of thermal-alkaline pretreatment conditions and then utilize this optimized pretreatment condition in an adFO-MBR to determine its performance compared to the former pretreatment conditions.

2. MATERIALS AND METHODS

2.1. Experimental design for pretreatment optimization

In this study, batch experiments were carried out for the purpose of pretreatment optimization. Conical flasks with an effective volume of 400 mL were used in batch experiments. Raw sludge of the batch experiments was either untreated, treated by ultrasound, or treated by thermal-alkaline, respectively. The raw sludge treated by thermal-alkaline was conducted by orthogonal testing and the experimental conditions are shown in Table 1. The raw sludge for reactor feeding was obtained from Yongfeng wastewater treatment plant (Beijing, China) and the seed sludge was from a conventional anaerobic digestion reactor in the laboratory where the experiments were conducted. Table 2 lists the characteristics of the seed and the substrate sludge.

Table 1 | Orthogonal experimental design for thermal-alkaline pretreatment

	Factor number			
Test number	**1 (Temperature)**	**2 (Heating time)**	**3 (pH)**	**4 (Alkaline)**
1	Raw sludge untreated			
2	Sludge treated by ultrasound for 30 min			
3	1 (70 °C)	1 (30 min)	1 (8)	1 (NaOH)
4	1 (70 °C)	2 (60 min)	2 (9)	2 (KOH)
5	1 (70 °C)	3 (90 min)	3 (10)	3 ($Ca(OH)_2$)
6	2 (80 °C)	1 (30 min)	2 (9)	3 ($Ca(OH)_2$)
7	2 (80 °C)	2 (60 min)	3 (10)	1 (NaOH)
8	2 (80 °C)	3 (90 min)	1 (8)	2 (KOH)
9	3 (90 °C)	1 (30 min)	3 (10)	2 (KOH)
10	3 (90 °C)	2 (60 min)	1 (8)	3 ($Ca(OH)_2$)
11	3 (90 °C)	3 (90 min)	2 (9)	1 (NaOH)

Table 2 | Characteristics of the raw sludge and the seed sludge

Sludge type	pH	Conductivity (mS/cm)	TS (%)	VS (%)	VS/TS (%)	SCOD (mg/L)
Raw sludge	6.88 ± 0.05	1.14 ± 0.13	4.34 ± 0.03	2.34 ± 0.01	53.96 ± 0.33	274.65 ± 3.75
Inoculum	6.95 ± 0.05	2.88 ± 0.22	3.28 ± 0.11	1.61 ± 0.11	49.04 ± 1.75	366.20 ± 10.00

Before the experiment, the raw sludge and the seed sludge were mixed at a ratio of 1:1 (calculated by volatile solid) and then blown by nitrogen for 5 min to remove oxygen. The flask-tests were numbered in the following order: 1-raw sludge untreated, 2-sludge treated by ultrasound for 30 min, and 3–11 were tests designed with the orthogonal method (shown in Table 1). The frequency of ultrasound used for pretreatment is 40 kHz and the working time was determined based on references and experimental results from pre-studies. The biogas produced was collected by sampling bags attached to the bottles. In addition, 8 mL of the sludge were sampled every two days for analysis. The batch experiment lasted for 20 days.

In order to study the results from orthogonal tests, the range analysis is utilized in this study. Range analysis is a statistical method to determine the sensitivity of factors to experimental results on the basis of orthogonal experiments. First, we define K_{ij} and k_{ij}. K_{ij} represents the total of an assessment parameter under level i of factor j and k_{ij} represents the average of an assessment parameter under level i of factor j. Then, the range R_j, i.e., the difference between the maximum and minimum average values under a certain level of factors in the j column could be calculated according to Equation (1) (Peng *et al.* 2006):

$$R_j = max(k_{1j}, k_{2j}, \ldots, k_{ij},) - min(k_{1j}, k_{2j}, \ldots, k_{ij},) \tag{1}$$

2.2. Reactor, feed sludge, and inoculum

In this study, ADFO-MBR had an effective volume of 1.0 L and the organic loading rate of it was kept at 1.50 $gVS \cdot L^{-1} \cdot d^{-1}$ throughout the test. The configuration of ADFO-MBR is shown in Figure 1.

In the start-up period, the feeding sludge for ADFO-MBR was diluted with deionized water to make the TS around 4.27% (w/w). This start-up period lasted for about 20–35 days until the measured parameters such as TS, volatile solid (VS) degradation, and biogas yield remained stable or fluctuated in a small range. After this start-up period, the solid content in the reactor was about 3.5% and gradually raised to around 7% by drawing the permeate out through a forward osmosis membrane when keeping using the feed sludge with 4.27% TS. For ADFO-MBR, the HRT was 18 days during either start-up period or TS-increasing period.

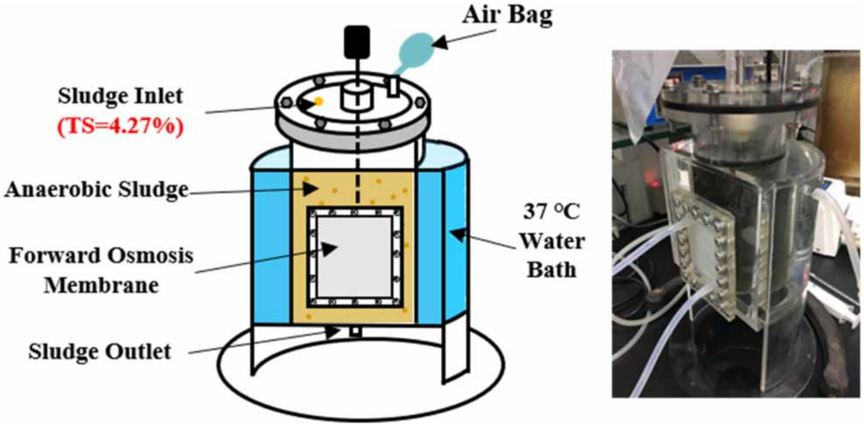

Figure 1 | Configuration of the ADFO-MBR for sludge AD.

2.3. Analytical methods

The sludge of the batch experiment and ADFO-MBR were sampled every two days for the analysis of methane production, pH value, conductivity, VFAs and SCOD. For ADFO-MBR, sludge TS and VS were also measured every two days.

Methane content of the biogas was measured by a gas chromatograph (GC) (Agilent Technologies 7890B, USA). The pH value was determined by a pH meter (METTLER TOLEDO, Switzerland). The conductivity was measured by a conductivity meter (Shanghai INESA Scientific Instrument Co., Ltd, China). TS and VS of AD sludge were measured by the weight difference method. To analyze volatile fatty acids (VFAs), the sludge samples taken from the reactors were centrifuged at 10,000 rpm for 10 min. Then the supernatant was passed through a microfiber filter (0.45 μm) and the filtrate was acidified with phosphoric acid to adjust the pH to approximately 2.0 before VFAs were analyzed by a GC (Shimadzu 2010Pro, Japan) with flame ionization detector. Soluble chemical oxygen demand (SCOD) was determined by potassium dichromate method using a multi-parameter water quality analyzer (Lianhua Technology, China) (APHA 2021). To analyze this parameter, the AD sludge samples were first centrifuged at 10,000 rpm for 10 min and then the supernatant was passed through a microfiber filter (0.45 μm). The particle size distribution of sludge samples was determined with a laser particle size analyzer (Mastersizer 3000, Malvern, UK).

3. RESULTS AND DISCUSSION

3.1. Effects of different pretreatment approaches on sludge anaerobic digestion

Figure 2(a)–2(c) plots the concentrations of SCOD at the first, fourth and tenth days of the reaction respectively. Figure 2(a) shows the SCOD concentration on the first day, that is, the conditions of cell lysis under different pretreatment conditions. As can be seen from Figure 2(a) that the SCOD concentration of sludge treated with thermal-alkaline (test numbers 3–11) were all higher than control (test numbers 1 and 2), indicating that the pretreatment of thermal-alkaline enhanced the release of soluble matters in sludge cells (Tian *et al.* 2018). Furthermore, the SCOD concentration of the sludge treated by NaOH to adjust pH to 9 (test number 11) or 10 (test number 7) were higher than others (>9,000 mg/L), revealing that NaOH had a better effect in the cell solubilization. Figure 2(b) shows the changes of SCOD under different pretreatment conditions at the fourth day of the reaction. It can be seen that SCOD showed a significant downward trend on the fourth day of the reaction, and SCOD decreased by 82.9% when the number 3 (NaOH adjusted pH to 8 and heated at 70 °C for 30 min) was the best to remove SCOD. The untreated sludge (No. 1) SCOD is still elevated. Figure 2(c) shows the concentration of SCOD under different pretreatment conditions on the last day of the reaction. It can be seen that the SCOD removal effect of sludge treated with NaOH adjusted to pH 9 (test number 11) or 10 (test number 7) was better than other pretreatment conditions, and the SCOD decreased by 93.1 and 91.3%, respectively.

Figure 2(d) shows the concentration of VFAs on the first day of reaction under different pretreatment conditions. It can be seen that the VFAs concentration of the sludge after thermo-alkaline treatment (test numbers 3–11) was higher than that of the control (test numbers 1 and 2). Its concentration trend was roughly the same as SCOD. It has been reported that the hydrolysis rate could be increased under alkaline conditions and thus more soluble substrates be produced, finally

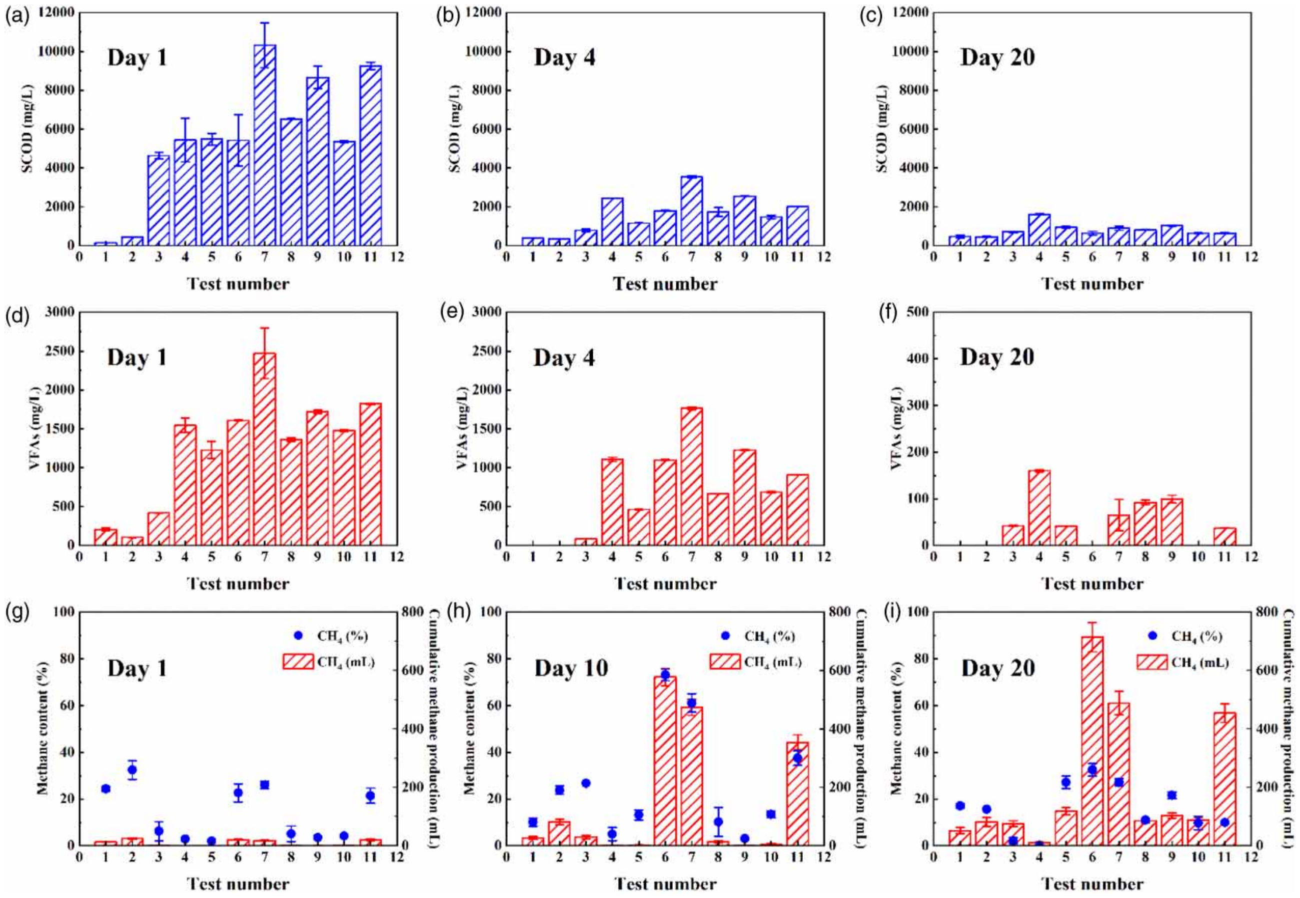

Figure 2 | Variation of different parameters along with fermentation time and testing conditions. SCOD: (a) day 1, (b) day 4, and (c) day 20. VFAs: (d) day 1, (e) day 4, and (f) day 20. Methane production: (g) day 1, (h) day 4, and (i) day 20.

accelerating the acidification process (Yuan *et al.* 2006). This not only showed that the production of VFAs was high, but also consistent with the results of SCOD in the previous paragraph. Figure 2(e) shows the changes of VFAs under different pretreatments on the fourth day of the reaction, indicating that the concentration of VFAs decreased during the reaction process, indicating that VFAs were consumed during the anaerobic digestion of sludge. Figure 2(f) shows the VFAs concentration at the end of the reaction on the day that almost all of the acid in the vials was consumed. In addition, similar to the results of the previous paragraph, the consumption of VFAs of the sludge treated by NaOH to adjust pH to 9 (test number 11) or 10 (test number 7) were bigger than other pretreatment conditions.

Figure 2(g)–2(i) shows the methane production at different stages in the batch experiment. Obviously, on the first day, test numbers 1, 2, 6, 7, and 11 started to produce methane. On the tenth day, it can be seen from Figure 2(h) that sludge treated with $Ca(OH)_2$ and pH adjusted to 9 (test number 6) and NaOH, pH adjusted to 9 (test number 11) and 10 (test number 7) had higher cumulative gas production, reaching 577.77 mL, 354.41 mL and 474.40 mL, respectively, which were the three better treatment conditions in this experiment. As shown in Figure 2(i), methane production on the last day, it can be seen that under the three better pretreatment conditions, the cumulative methane production raised to 450–720 mL, which was much better than the cumulative methane production of other conditions. Methane content increased to 30–65% under these conditions. As a result, the effects of methane production were best when the sludge was treated by $Ca(OH)_2$, pH adjusted to 9 (test number 6) and by NaOH, pH adjusted to 9 (test number 11) and 10 (test number 7).

Taking the sludge treated by NaOH to adjust pH to 9 (test number 11) and 10 (test number 7) where the effects of cell solubilization were best as two examples, the particle size of them were analyzed compared to the sludge untreated (test number 1) and the results were shown in Figure 3. As can be seen from Figure 3(a) and 3(b), the particle size of the sludge treated by thermal-alkaline (test numbers 7 and 11) and the sludge untreated (test number 1) all ranged from

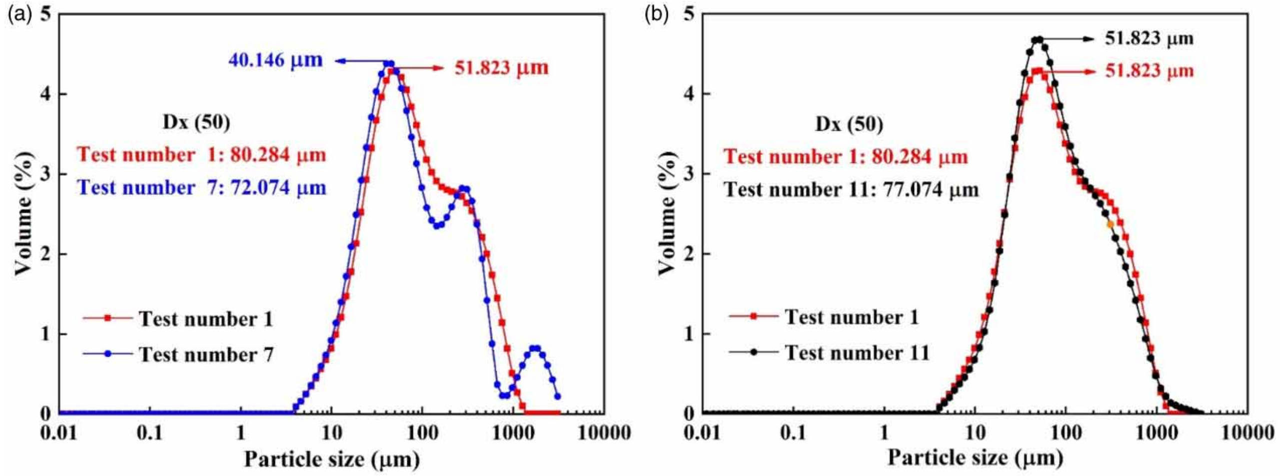

Figure 3 | Comparison of particle size distribution and median particle size between (a) test #1 and test #7, and (b) test #1 and test #11.

0.01 μm to 3,500 μm. However, when the sludge particle size was below 100 μm, the sludge particle size distribution under thermal-alkaline pretreatment conditions (test numbers 7 and 11) was more concentrated than that of the sludge untreated (test number 1). This phenomenon was in accordance with a previous study (Huang *et al.* 2019). In particular, when the pH was adjusted to 10 with NaOH in test 7, two peaks in sludge particle size were observed in the range of 100 μm to 3,500 μm (Figure 3(a)). In a previous study, sludge was hydro-thermally pretreated by using a set of conditions (160 °C, 60 min, pH 10) and two peaks on the curve of particle size distribution were also observed (Li *et al.* 2017). Jin *et al.* (2009) found that high doses of alkali treatment may cause flocculation of cell particles and the formation of flocs, resulting in an increase in particle size. Furthermore, after the pretreatment of thermal-alkaline (test numbers 7 and 11), the medium particle size of the sludge was smaller than that of the sludge untreated (test number 1). Esposito *et al.* found that larger sludge particle size results in slower decomposition and acidification, and the overall efficiency of COD removal decreases (Esposito *et al.* 2011). Combining this result with the result of SCOD, it can be concluded that thermal-alkaline pretreatment promoted cell solubilization to some extent.

3.2. Optimization of pretreatment conditions

Since the purpose of thermal-alkaline pretreatment is to enhance cell solubilization and ultimately promote methane production, we conducted the optimization of pretreatment conditions based on the effects of cell solubilization and methane production as shown in Tables 3 and 4, respectively. The optimum condition in each factor is the corresponding level of the maximum value of K or k. Moreover, the combination of the optimum conditions in all factors is the optimum pretreatment condition in a certain metric. Furthermore, the bigger the value of range R is, the more important the factor is. Hence, based on the effects of cell solubilization, the optimum combination of pretreatment condition was 90 °C, 90 min, pH = 10, NaOH; the suboptimal combination was 80 °C, 60 min, pH = 9, KOH. However, based on the effects of methane production, the optimum combination of pretreatment condition was 80 °C, 30 min, pH = 9, NaOH; the suboptimal combination was 90 °C, 90 min, pH = 10, $Ca(OH)_2$. In addition, based on the effects of cell solubilization and methane production, temperature, pH and alkaline were all important factors. Under both of the two metrics, NaOH was the most suitable alkaline, while the other three factors differed. In terms of heating temperature, the higher the heating temperature was, the better the effects of cell solubilization were. Moreover, a higher temperature also increased the methane production. Therefore, 90 °C was selected as the most suitable heating temperature. When the pH value was 9, the system achieved the best effects of methane production. In addition, the amount of alkali input is relatively small, and the cell lysis effect is also ideal. Thus, pH = 9 was selected as the most suitable pH value. Compared with other factors, heating time only has weak influence on SCOD concentration and methane production based on R values in Tables 3 and 4. Considering K_i, 60 min of heating should be selected in terms of SCOD concentration and energy input for heating; and 30 min of heating was the best in terms of methane production. According to results from single factor experiments conducted, a too short heating time was not good for the cell solubilization

Table 3 | Optimization of pretreatment conditions based on the effects of cell solubilization

	Factor number				
Test number	1 Temperature	2 Heating time	3 pH	4 Alkaline	SCOD (mg/L)
3	1 (70 °C)	1 (30 min)	1 (8)	1 (NaOH)	4,635
4	1 (70 °C)	2 (60 min)	2 (9)	2 (KOH)	5,433
5	1 (70 °C)	3 (90 min)	3 (10)	3 ($Ca(OH)_2$)	5,478
6	2 (80 °C)	1 (30 min)	2 (9)	3 ($Ca(OH)_2$)	5,417
7	2 (80 °C)	2 (60 min)	3 (10)	1 (NaOH)	10,324
8	2 (80 °C)	3 (90 min)	1 (8)	2 (KOH)	6,517
9	3 (90 °C)	1 (30 min)	3 (10)	2 (KOH)	8,654
10	3 (90 °C)	2 (60 min)	1 (8)	3 ($Ca(OH)_2$)	5,358
11	3 (90 °C)	3 (90 min)	2 (9)	1 (NaOH)	9,255
K_1	15,546	18,706	16,510	24,214	
K_2	22,258	21,115	20,105	20,604	
K_3	23,267	21,250	24,456	16,253	
k_1	5,182	6,235.33	5,503.33	8,071.33	
k_2	7,419.33	7,038.33	6,701.67	6,868	
k_3	7,755.67	7,083.33	8,152	5,417.67	
R	2,573.67	848	2,648.67	2,653.67	

Table 4 | Optimization of pretreatment conditions based on the effects of methane production

	Factor number				
Test number	1 Temperature	2 Heating time	3 pH	4 Alkaline	Cumulative methane production (mL)
3	1 (70 °C)	1 (30 min)	1 (8)	1 (NaOH)	75.92
4	1 (70 °C)	2 (60 min)	2 (9)	2 (KOH)	10.95
5	1 (70 °C)	3 (90 min)	3 (10)	3 ($Ca(OH)_2$)	118.40
6	2 (80 °C)	1 (30 min)	2 (9)	3 ($Ca(OH)_2$)	713.77
7	2 (80 °C)	2 (60 min)	3 (10)	1 (NaOH)	488.26
8	2 (80 °C)	3 (90 min)	1 (8)	2 (KOH)	86.24
9	3 (90 °C)	1 (30 min)	3 (10)	2 (KOH)	103.50
10	3 (90 °C)	2 (60 min)	1 (8)	3 ($Ca(OH)_2$)	87.62
11	3 (90 °C)	3 (90 min)	2 (9)	1 (NaOH)	454.53
K_1	205.27	893.19	249.78	1,018.71	
K_2	1,288.28	586.83	1,179.26	200.70	
K_3	645.65	659.17	710.16	919.79	
k_1	68.42	297.73	83.26	339.57	
k_2	429.43	195.61	393.09	66.90	
k_3	215.22	219.72	236.72	306.60	
R	361.00	102.12	309.83	272.67	

as well as the methane production. Consequently, a moderate heating time 60 min was selected as the most suitable heating time. As a result, the ultimately selected optimum combination of pretreatment condition was 90 °C, 60 min, pH = 9, NaOH.

3.3. Effect of optimized pretreatment approach on the performance of ADFO-MBR

The optimal pretreatment condition selected in section 3.2 was applied to ADFO-MBR and the experimental performance was studied. The operating data of ADFO-MBR with sludge treated by ultrasound for 30 min as the pretreatment condition served as the comparison for this 100 d's performance of sludge treated by the optimal pretreatment condition.

During the 100 d's performance of ADFO-MBR, the pH value of the sludge treated by thermal-alkaline ranged from 7.2 to 7.5. However, the pH value of the sludge treated by ultrasound ranged from 7.0 to 7.4. The pH values of them were all in the optimal pH range for anaerobic digestion (6.8–7.5) (Mao *et al.* 2017). The conductivity of the sludge treated by thermal-alkaline and ultrasound ranged from 5.4–7.8 mS/cm and 2.4–5.4 mS/cm, respectively. As a result of the addition of alkaline, the conductivity of the sludge treated by thermal-alkaline was higher than that of the sludge treated by ultrasound, which was consistent with the results from batch experiments, the conductivity of which were described in the supplementary material. The increase of the conductivity of both of the two pretreatment conditions could be explained by the reverse salt flux of the draw solution $MgCl_2$ (Zhao *et al.* 2018).

Figure 4(a) shows that the SCOD concentration of the sludge treated by thermal-alkaline was higher than that of the sludge treated by ultrasound, indicating a better performance of cell solubilization of the sludge treated by thermal-alkaline. This phenomenon was also identical to the results obtained in section 3.1. Figure 4(b) shows that the VFAs concentration of the sludge treated by both of the two pretreatment conditions showed a trend of first decreasing and then stabilizing. This phenomenon could be illustrated by the consumption of VFAs during the sludge anaerobic digestion process. However,

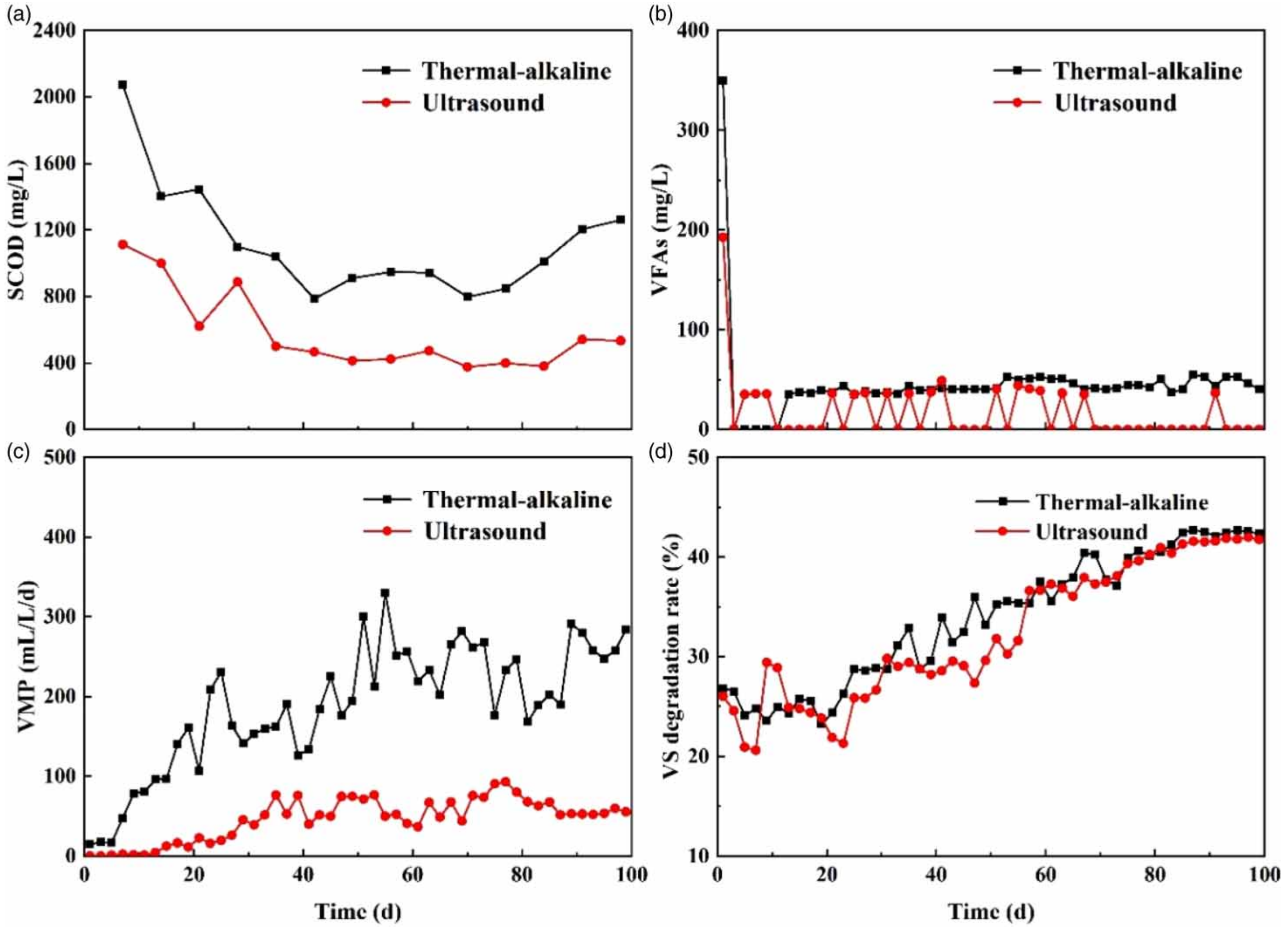

Figure 4 | Variation of SCOD (a), VFAs (b), VMP (c) and VS degradation rate (d) during the operation of ADFO-MBR.

the VFAs concentration of sludge treated by thermal-alkaline was higher than that of the sludge treated by ultrasound during the operation of ADFO-MBR, indicating that the acidification process was accelerated by the pretreatment of thermal-alkaline, which was also in consistent with the results drawn in section 3.1.

Figure 4(c) shows the volumetric methane production (VMP) of the sludge treated by different pretreatment conditions during the operation of ADFO-MBR. It can be seen that both curves showed a trend of first increasing and then stabilizing. Obviously, sludge treated by thermal-alkaline showed a higher VMP than that of the sludge treated by ultrasound. The VMP of the sludge treated by thermal-alkaline was maintained at around 200–300 mL/L/d, which was 2 or 3 times that of the sludge treated by ultrasound.

Figure 4(d) plots the variation of the VS degradation rate during the operation of ADFO-MBR. It can be seen that the VS degradation rate under both of the two pretreatment conditions showed a trend of first increasing then stabilizing. Comparing the two pretreatment conditions, the VS degradation rate of the sludge treated by thermal-alkaline was a little higher than that of the sludge treated by ultrasound. The VS degradation rate of the sludge treated by thermal-alkaline and ultrasound was stabled at approximately 42% and 41%, respectively, which is at a relatively high level if compared with other reported cases. The VS degradation rate in sludge anaerobic digestion ranged from 19% to 45% after a thermal alkali pretreatment. Lin *et al.* conducted anaerobic digestion after thermal alkali pretreatment (Lin *et al.* 1997). In another similar study, the VS reduction rate was in the range of 15.4–40.0% (Nazari *et al.* 2017). As a result, it can be concluded that under the optimized thermal-alkaline pretreatment condition, the sludge VS degradation rate was higher and had a better anaerobic digestion performance.

3.4. Analysis of membrane fouling during the operation of ADFO-MBR

Figure 5 shows the membrane flux of ADFO-MBR during the operation under the pretreatment of thermal-alkaline and ultrasound. The concentration of the draw solution $MgCl_2$ was gradually increased from 0.5 mol/L to 1.0 mol/L and then to 1.25 mol/L. The membrane flux gradually decreased at a certain concentration of $MgCl_2$, indicating that the forward osmosis membrane was gradually fouled during the operation. Moreover, the initial membrane flux was increased with the increase of the concentration of $MgCl_2$. The fluctuation of the membrane flux of ADFO-MBR during the operation under the pretreatment of thermal-alkaline and ultrasound was similar to each other. It seems that 1.25 mol/L $MgCl_2$ was a better concentration of the draw solution for the operation of ADFO-MBR, which lasted for approximately 40 days. During which period, the membrane flux was stable at around 0.2 $L/m^2/h$ and 0.3 $L/m^2/h$ under the pretreatment of thermal-alkaline and ultrasound, respectively.

4. CONCLUSION

In view of the problems that limit the performance of sludge anaerobic digestion, such as poor cell disintegration and low organic loading rate, parameters of a thermal-alkaline pretreatment were optimized with orthogonal test method. Considering

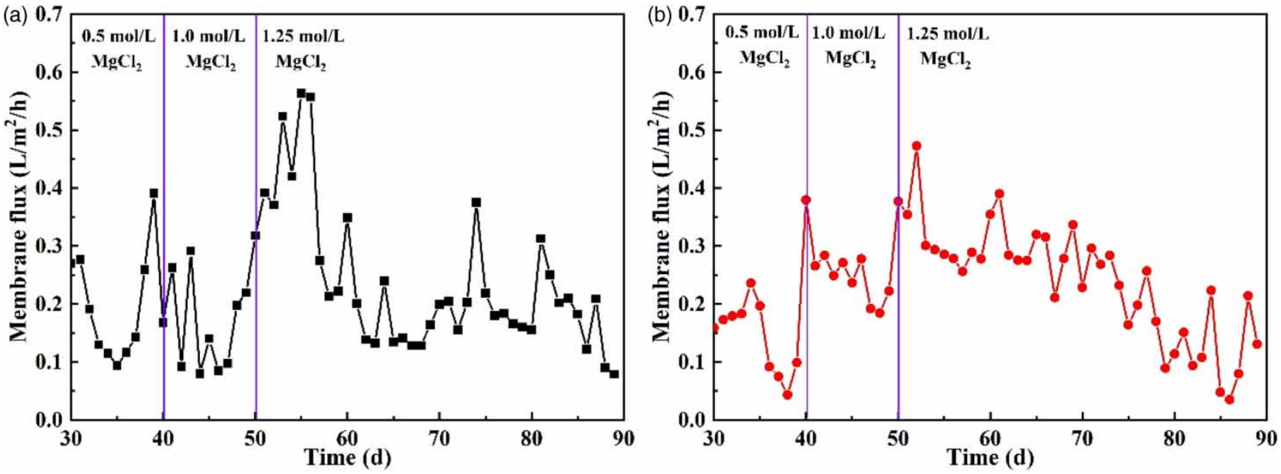

Figure 5 | Membrane flux of ADFO-MBR during the operation under the pretreatment of thermal-alkaline (a) and ultrasound (b).

effects on SCOD and methane production comprehensively, the selected set of pretreatment conditions is heating at 90 °C for 60 min and adjusting pH to 9 by NaOH. When the pretreated sludge was applied to an ADFO-MBR for a long-term operation test, a number of anaerobic digestion performance indicators have been improved. The removal rate of SCOD reached 93.13%, and the volumetric methane yield of the reactor reached 200–300 mL/L/d, which is 2–3 times higher than that used ultrasonic pretreated sludge as feeds. Application of the thermal-alkaline pretreatment to the feeding sludge for an ADFO-MBR is beneficial to the cell disintegration, the release of organic matter, and a higher methane production efficiency. This study provides a feasible pretreatment option for the practice of a long-term operation of ADFO-MBR.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Adekunle, K. F. & Okolie, J. A. 2015 A review of biochemical process of anaerobic digestion. *Advances in Bioscience and Biotechnology* **6**, 205–212.

APHA/AWWA/WEF 2021 *Standard Methods for the Examination of Water and Wastewater*, 22th edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.

Appels, L., Dewil, R., Baeyens, J. & Degrève, J. 2008 Ultrasonically enhanced anaerobic digestion of waste activated sludge. *International Journal of Sustainable Energy* **1**, 94–104.

Chen, H., Yi, H., Li, H., Guo, X. & Xiao, B. 2020 Effects of thermal and thermal-alkaline pretreatments on continuous anaerobic sludge digestion: performance, energy balance and, enhancement mechanism. *Renewable Energy* **147**, 2409–2416.

Chiappero, M., Demichelis, F., Lin, X., Liu, C., Frigon, D. & Fiore, S. 2019 Investigation of pre-treatments improving low-temperature anaerobic digestion of waste activated sludge. *Process Safety and Environmental Protection* **131**, 28–37.

Choi, J. M., Han, S. K. & Lee, C. Y. 2018 Enhancement of methane production in anaerobic digestion of sewage sludge by thermal hydrolysis pretreatment. *Bioresource Technology* **259**, 207–213.

Deepanraj, B., Sivasubramanian, V. & Jayaraj, S. 2014 Biogas generation through anaerobic digestion process-an overview. *Research Journal of Chemistry and Environment* **18** (5), 80–93.

Du, J., Qian, Y., Xi, Y. & Lü, X. 2019 Hydrothermal and alkaline thermal pretreatment at mild temperature in solid state for physicochemical properties and biogas production from anaerobic digestion of rice straw. *Renewable Energy* **139**, 261–267.

Esposito, G., Frunzo, L., Panico, A. & Porozzi, F. 2011 Modelling the effect of the OLR and OFMSW particle size on the performances of an anaerobic co-digestion reactor. *Process Biochemical* **46**, 557–565.

Huang, Y., Wang, Y., Liu, S., Huang, W., He, L. & Zhou, J. 2019 Enhanced hydrolysis-acidification of high-solids and low-organic-content sludge by biological thermal-alkaline synergism. *Bioresource Technology* **294**, 122234.

Jeong, S. Y., Chang, S. W., Ngo, H. H., Guo, W., Nghiem, L. D., Banu, J. R., Jeon, B. H. & Nguyen, D. D. 2019 Influence of thermal hydrolysis pretreatment on physicochemical properties and anaerobic biodegradability of waste activated sludge with different solids content. *Waste Management* **85**, 214–221.

Jin, Y. Y., Li, H., Mahar, R. B., Wang, Z. Y. & Nie, Y. F. 2009 Combined alkaline and ultrasonic pretreatment of sludge before aerobic digestion. *Journal of Environmental Sciences* **21**, 279–284.

Jin, B., Wang, S., Xing, L., Li, B. & Peng, Y. 2016 Long term effect of alkali types on waste activated sludge hydrolytic acidification and microbial community at low temperature. *Bioresource Technology* **200**, 587–597.

Kor-Bicakci, G. & Eskicioglu, C. 2019 Recent developments on thermal municipal sludge pretreatment technologies for enhanced anaerobic digestion. *Renewable and Sustainable Energy Reviews* **110**, 423–443.

Li, C., Wang, X., Zhang, G., Yu, G., Lin, J. & Wang, Y. 2017 Hydrothermal and alkaline hydrothermal pretreatments plus anaerobic digestion of sewage sludge for dewatering and biogas production: bench-scale research and pilot-scale verification. *Water Research* **117**, 49–57.

Li, X., Guo, S., Peng, Y., He, Y., Wang, S., Li, L. & Zhao, M. 2018 Anaerobic digestion using ultrasound as pretreatment approach: changes in waste activated sludge, anaerobic digestion performances and digestive microbial populations. *Biochemical Engineering Journal* **139**, 139–145.

Lin, J. G., Chang, C. N. & Chang, S. C. 1997 Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilization. *Bioresource Technology* **62**, 85–90.

Liu, X., Xu, Q., Wang, D., Yang, Q., Wu, Y., Li, Y., Fu, Q., Yang, F., Liu, Y., Ni, B. J., Wang, Q. & Li, X. 2019 Thermal-alkaline pretreatment of polyacrylamide flocculated waste activated sludge: process optimization and effects on anaerobic digestion and polyacrylamide degradation. *Bioresource Technology* **281**, 158–167.

Liu, X. R., Fu, Q. Z., Liu, Z. Y., Zeng, T. J., Du, M. T., He, D. D., Lu, Q., Ni, B. J. & Wang, D. B. 2021 Alkaline pre-fermentation for anaerobic digestion of polyacrylamide flocculated sludge: simultaneously enhancing methane production and polyacrylamide degradation. *Chemical Engineering Journal* **425**, 131407.

Mao, C., Wang, X., Xi, J., Feng, Y. & Ren, G. 2017 Linkage of kinetic parameters with process parameters and operational conditions during anaerobic digestion. *Energy* **135**, 352–360.

Nazari, L., Yuan, Z. S., Santoro, D., Sarathy, S., Ho, D., Batstone, D., Xu, C. & Ray, M. B. 2017 Low-temperature thermal pre-treatment of municipal wastewater sludge: process optimization and effects on solubilization and anaerobic degradation. *Water Research* **113** (15), 111–123.

Peng, J. Y., Dong, F. Q., Xu, Q. W., Xu, Y. W., Qi, Y., Han, X., Xu, L., Fan, G. R. & Liu, L. X. 2006 Orthogonal test design for optimization of supercritical fluid extraction of daphnoretin, 7-methoxy-daphnoretin and 1,5-diphenyl-1-pentanone from *Stellera chamaejasme* L. and subsequent isolation by high-speed counter-current chromatography. *Journal of Chromatography A* **1135** (2), 151–157.

Roebuck, P., Kennedy, K. & Delatolla, R. 2019 Ultrasonic pretreatment for anaerobic digestion of suspended and attached growth sludges. *Water Quality Research Journal* **54** (4), 265–277.

Tian, X., Ng, W. J. & Trzcinski, A. P. 2018 Optimizing the synergistic effect of sodium hydroxide/ultrasound pretreatment of sludge. *Ultrasonics – Sonochemistry* **48**, 432–440.

Wang, Q., Sun, J., Liu, S., Gao, L., Zhou, X., Wang, D., Song, K. & Nghiem, L. D. 2019a Free ammonia pretreatment improves anaerobic methane generation from algae. *Water Research* **162**, 269–275.

Wang, S., Yu, S., Lu, Q., Liao, Y., Li, H., Sun, L., Wang, H. & Zhang, Y. 2019b Development of an alkaline/acid pre-treatment and anaerobic digestion (APAD) process for methane generation from waste activated sludge. *Science of The Total Environment* **708**, 134564.

Yang, G., Zhang, G. & Wang, H. 2015 Current state of sludge production, management, treatment and disposal in China. *Water Research* **78**, 60–73.

Yang, Y., Cheng, G., Li, Y., Wang, T., Li, F. & Huang, W. 2018 Effect of agitation pretreatment on anaerobic digestion of swine manure. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **41** (1), 122–128.

Yuan, H., Chen, Y., Zhang, H., Jiang, S., Zhou, Q. & Gu, G. 2006 Improved bioproduction of Short-Chain Fatty Acids (SCFAs) from excess sludge under alkaline conditions. *Environmental Science and Technology* **40**, 2025–2029.

Zhang, Y., Xu, S., Cui, M. & Wong, J. W. C. 2019a Effects of different thermal pretreatments on the biodegradability and bioaccessibility of sewage sludge. *Waste Management* **94**, 68–76.

Zhang, Y., Zhang, L., Liu, H., Gong, L., Jiang, Q., Liu, H. & Fu, B. 2019b Carbon dioxide sequestration and methane production promotion by wollastonite in sludge anaerobic digestion. *Bioresource Technology* **272**, 194–201.

Zhao, J., Li, Y., Pan, S., Tu, Q., Dang, W., Wang, Z. & Zhu, H. T. 2018 Effects of magnesium chloride on the anaerobic digestion and the implication on forward osmosis membrane bioreactor for sludge anaerobic digestion. *Bioresource Technology* **268**, 700–707.

Zhao, J., Li, Y., Pan, S., Tu, Q. & Zhu, H. T. 2019 Performance of a forward osmotic membrane bioreactor for anaerobic digestion of waste sludge with increasing solid concentration. *Journal of Environmental Management* **246**, 239–246.

Zhen, G., Lu, X., Kato, H., Zhao, Y. & Li, Y. Y. 2017 Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: current advances, fullscale application and future perspectives. *Renewable and Sustainable Energy Reviews* **69**, 559–577.

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