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Impact of hydrothermal pre-treatment on the anaerobic digestion of different solid–liquid ratio sludges and kinetic analysis

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This study is an assessment of hydrothermal pre-treatment (HTP) of different solid–liquid ratio (SLR) sewage sludge for enhancement of biogas production by anaerobic digestion. Anaerobic digestion efficacy was investigated by biochemical methane potential (BMP) tests and kinetic analyses. The results indicated that the solid–liquid ratio (SLR) of sludge could influence the COD solubilization and the concentration of volatile fatty acids (VFAs) after HTP. BMP tests revealed that HTP could improve the final methane yield. For the different solid–liquid ratios (5%, 8%, 10%, 12% and 15%) of sludge after HTP, the methane contents were found to be 64%, 66%, 62%, 61% and 60%, respectively. The optimum solid–liquid ratio was found to be 8%, and its cumulative biogas yield was 425.57 N ml g^{-1} VS. The modified Gompertz model and Logistic model were used for kinetic study of biogas production. Kinetic study results showed that the experimental data could be fitted with the two models and the modified Gompertz model was better fitted with the experimental data than the Logistic model. These findings proved that choosing an appropriate solid–liquid ratio for HTP could effectively improve the anaerobic digestion process of sewage sludge.

1. Introduction

Bioenergy recovery from organic waste has been considered as an effective way to replace depleted fossil energy.[1–3] The reason is that it can decrease the use of fossil energy and avoid the environment pollution resulting from the undisposed waste.[4,5] Sewage sludge as an organic byproduct, discharged from sewage treatment plants, has enormous potentiality for bioenergy recovery because of its increasing production. Anaerobic digestion has been widely used to reduce the sludge volume and also produce biogas for power generation from the digested sludge.[6,7] Compared with other techniques, anaerobic digestion has many advantages like lower cost, lower energy consumption, and stable operation.[8]

Anaerobic digestion contains three biochemical reaction stages: hydrolysis fermentation stage – hydrolytic bacteria converts complex organic compounds to simple organic matters; acetogenesis stage – acidogenic bacteria transforms monomers into acetic acid and hydrogen; methanogenesis – methanogens used the product of the first two stages through a series of reactions to produce methane.[9,10] Hydrolysis is the rate-limiting step of anaerobic digestion due to the extracellular polymeric substances of the microorganisms and low biodegradability of cell walls.[11] However, many pre-treatment technologies can be used to improve the hydrolysis step of anaerobic digestion. Methane production, dewaterability, solid reduction, and pathogen removal can be enhanced for using different pre-treatment technologies.[12,13]

In order to enhance the performance of anaerobic digestion, several pre-treatment technologies have been considered to increase the physicochemical characteristics of sewage sludge. Various methods were investigated by many researchers, such as biological pre-treatment,[14] physical (ultrasonic, microwave *et al.*) pre-treatment,[15–17] chemical (ozone oxidation, thermal and hydrolysis *et al.*) pre-treatment.[12,18–20] Such sludge pre-treatment technologies are working on the principle of disintegration of cell walls and causing lysis, leading to the release of intracellular organic matter that become more easy to be used for anaerobic microorganisms. Among thermo-chemical pre-treatment methods, hydrothermal pre-treatment (HTP) has significant enhancement effect on achieving organic material degradation and anaerobic digestion performance.[21] HTP is under high temperature and pressure to achieve the cell solubilization and destruction of sewage sludge efficiently.[22] Many researchers have been studied the influence on solid–liquid ratio (SLR),[23] temperature and time for HTP of sludge,[24–26] applied temperature range from 100 °C to 280 °C for fifteen minutes to several hours.[27,28] They also proved that HTP was an effective method to increase methane production and reduced volatile solids (VS), with a relatively low energy input and being a more environmentally technology.

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In previous work, hydrothermal temperature and time had been proved to have influence on anaerobic digestion,[29] it found the optimal pre-treatment temperature and time was 160 °C for 60 min. Also there were few studies mentioned the relationship of different solid–liquid ratio (SLR) and biogas production. The SLR was related to moisture content of sludge after dewatering and the cost of sludge conditioning. This study was to use hydrothermal pre-treatment on different SLR sludge, discussed the sludge characteristics and anaerobic biodegradability. It was not obvious if a small gradient of SLR was used. So in this study set five groups of 5%, 8%, 10%, 12% and 15%. Biogas yield and methane content were obtained in the anaerobic biodegradability tests and the kinetic study was analyzed by the modified Gompertz model and Logistic model. The purpose of this experiment was to find the best solid–liquid ratio and provided the basis for industrial application.

2. Materials and methods

2.1. Sewage sludge characteristics

The sewage sludge sample was taken from the discharge of a horizontal spiral filter centrifuge in a municipal wastewater treatment plant in Qingdao, China. Primary characteristics of different SLR sludge (such as total solid content (TS), volatile solid content (VS), total COD (TCOD), soluble COD (SCOD), ammonia nitrogen (NH_4-N)) were listed in Table 1. After that, the sewage sludge was stored at 4 °C to minimize impact of biological activity. Each experiment was repeated three times and a mean value was used in the study.

In the experiment, the SLR of the sludge was determined by

$$\text{SLR} = \frac{m \times (1 - \text{MC})}{m \times \text{MC} + W} \times 100\% \qquad (2\text{-}1)$$

While, m is the quantity of the sludge; MC is the sludge moisture content; W is the volume of distilled water.

2.2. Hydrothermal pre-treatment experiments

HTP experiments were performed using a 2000 ml lab-scale reactor. The reactor (Fig. 1) included a reactor body, heater, attemperator, and stirrer *et al.* For all experiments, a 1200 ml feedstock (sludge and water mixture) was loaded into the reactor. The experiment operating temperature was 160 °C, the pressure of HTP was 0.8 MPa, and the reaction time was 60 min. The samples in the reactor were mixed using an agitator stirring at 220 rpm. The steam was discharged from the pressure reducing valve and the sludge was removed after the completion of hydrothermal pre-treatment reaction.
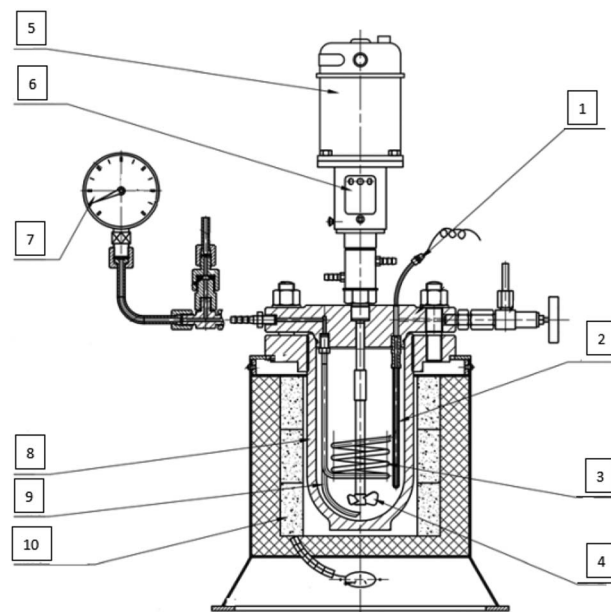

Fig. 1 The reactor of hydrothermal pre-treatment reaction. (1) Temperature measuring element. (2) Temperature measuring casing. (3) Cooling coil. (4) Stirring paddle. (5) Motor. (6) Magnetic drive system. (7) Pressure gage. (8) Reactor body. (9) Sampling tube. (10) Electric heating system.

2.3. Anaerobic biodegradability batch tests

Each sample from HTP and the raw sludge were performed by biochemical methane potential (BMP) tests. BMP tests for the experiments had also been performed in triplicate to guarantee the objectivity of the observed results. Each experiments inoculated with the active anaerobic sludge from the Qingdao sewage treatment plants in China and the inoculum was domesticated under 35 °C for 7 days before the BMP tests. When no significant gas production was observed, the inoculum was ready to be used. BMP tests were performed by the Bioprocess Control (Endeavor, Sweden AB). The Bioprocess Control consisted of an anaerobic digestion device, a biogas metering device, an attemperator, and ENDEAVOUR software. Anaerobic digestion device contained five sealed bottles of 2300 ml, each bottle had a rotating shaft for mixing and the operating temperature controlled by electro-thermostatic water cabinet was 35 °C. Biogas produced by the samples could be measured by the gas flowmeter. The ratio of inoculum VS to substrate VS was set at 1.5 according to the previous studies.[30,31] After the mixture was added, the bottles were flushed with N_2 to remove O_2. The blank digester containing only inoculum and untreated sludge was operated simultaneously with other digestion

Table 1 Characteristics of the different SLR sludge

Parameters	5%	8%	10%	12%	15%
VS (%)	1.93 ± 0.013%	4.03 ± 0.05%	5.32 ± 0.017%	6.43 ± 0.022%	7.72 ± 0.06%
TS (%)	3.44 ± 0.05%	7.64 ± 0.052%	9.99 ± 0.036%	12.34 ± 0.04%	14.33 ± 0.055%
SCOD (mg L^{-1})	8750 ± 47.13	15 578 ± 128.64	24 375 ± 327.29	26 897 ± 319.38	29 375 ± 309.96
TCOD (mg L^{-1})	30 625 ± 591.76	62 125 ± 316.56	96 250 ± 345.06	107 659 ± 376.93	113 750 ± 384.7
NH_4-N (mg L^{-1})	794 ± 8.544	1094 ± 13.45	1593 ± 8.54	1802 ± 14.73	2164 ± 14.8

experiments. Daily biogas production and cumulative biogas production were recorded by the ENDEAVOUR software.

The methane content of the biogas was analyzed by the gas chromatography (GC-1100, Pease Corporation, China). A volume of 0.5 ml of biogas was injected into the gas chromatography to measure biogas composition, detected proportions of methane and carbon dioxide. The temperatures of injector, detector and column were set 100 °C, 150 °C, and 120 °C, respectively. The gas composition was measured every two days. Digestion experiment was conducted until biogas production ceased.

2.4. Other analytical methods

The physical and chemical parameters VS, TS, total nitrogen (TN), NH_4-N, and COD were determined according to standard methods (Ministry of Environmental Protection, China (MEP), 2002). The SCOD was measured after centrifuging at 3000 rpm for 20 min and filtering the supernatant through membranes with mesh size of 0.45 μm. TNM and NH_4-NM were the total nitrogen and ammonia nitrogen analyzed from the mixed liquor. TN and NH_4-N were extraction from centrifuged the supernatant. The TCOD parameters were obtained from the mixed liquor. Volatile fatty acids (VFA) were analyzed using Pease gas chromatograph equipped with a flame ionization detector (FID) and a KB-FFAP column (30 m × 0.25 mm × 0.50 μm). Operating conditions were injector temperature 230 °C, FID temperature 230 °C, oven temperature program: 70–180 °C (20 °C min^{-1}), held for 5 min. Nitrogen was used as a carried gas. The VFAs were detected include acetic acid, propionic acid and butyric acid. The other acids such as lactic and valeric were very low, which had a little effect on the experimental results. The total VFAs was the sum of the three acids.

VS reduction (VSR) rate was determined by (2-2).[32]

$$VSR = \frac{VS_0/TS_0 - VS_1/TS_1}{VS_0/TS_0 - (VS_0/TS_0 \times VS_1/TS_1)} \times 100\% \quad (2-2)$$

While, VS_0/TS_0 is the VS/TS before the BMP tests, and VS_1/TS_1 is the VS/TS after the BMP tests.

Solubilization COD was determined by the formula (2-3).[33]

$$Solubilization\ COD = \frac{SCOD_T - SCOD_0}{TCOD_0 - SCOD_0} \times 100\% \quad (2-3)$$

While, $SCOD_0$ and $TCOD_0$ are the initial SCOD and TCOD of different SLR sludge, and $SCOD_T$ is the SCOD of different SLR sludge after HTP.

The different SLR sludge of TN and NH_4-N solubilization were determined by the formula (2-4).

$$Solubilization = \frac{A_T - A_0}{B_0 - A_0} \times 100\% \quad (2-4)$$

While, A_0 and B_0 are the initial TN (NH_4-N) and TNM (NH_4-NM) of different SLR sludge, and A_T is the TN (NH_4-N) of different SLR sludge after HTP.

2.5. Kinetic analysis

Kinetic analysis was used two kinetic models: the modified Gompertz model and the Logistic model. With the two models,

the maximum biogas production rate, biogas production potential of the substrate and the lag phase of their action could be determined with available experimental results. The experimental results obtained from all samples were fitted with the two kinetic models. And the two kinetic models described cumulative biogas production from batch digesters, assuming that biogas production was a function of bacterial growth.[34,35] The models expression was given by.[36]

$$P(t) = P \exp\left\{ -\exp\left[\frac{2.718 \times R_m}{P} \times (\lambda - t) + 1 \right] \right\} \quad (2-5)$$

$$P(t) = \frac{P}{1 + \exp\left[4R_m \times \frac{\lambda - t}{P} + 2 \right]} \quad (2-6)$$

While, $P(t)$ is cumulative biogas production; P is biogas production potential; R_m is maximum biogas production rate; λ is lag time.

In order to evaluate the models, the kinetic parameters of the samples were calculated using final prediction error (FPE),[37] correlation of determination (r^2)[38] and root mean square error (RMSE)[39] for this analysis.

$$R = \frac{\sum_{i=1}^{n}(z_i - \overline{z})(w_i - \overline{w})}{\sqrt{\sum_{i=1}^{n}(z_i - \overline{z})^2 \sum_{i=1}^{n}(w_i - \overline{w})^2}} \quad (2-7)$$

$$r^2 = R \quad (2-8)$$

$$RMSE = \sqrt[2]{\frac{1}{n}\sum_{i=1}^{n}(z_i - w_i)^2} \quad (2-9)$$

$$FPE = \frac{1 + p/n}{1 - p/n} \times \frac{1}{n} \times \sum_{i=1}^{n}\frac{1}{2}\left(\frac{z_i - w_i}{z_i}\right)^2 \quad (2-10)$$

While, z_i is the experimental value; w_i is the predicted value; n is the number of samples. P is the degree of freedom.

3. Results and discussion

3.1. Effect of HTP on different SLR sludge solubilization

3.1.1 COD solubilization. Compared with the raw sludge for different SLR, the SCOD was improved by 282.15%, 309.95%, 279.49%, 239.23% and 180.85% for SLR 5%, 8%, 10%, 12% and 15%, respectively, after HTP. The physicochemical property of the sludge was found to be improved and the concentrations of SCOD was enhanced after HTP.[40] Results from this study also indicated that the SLR significantly affected the SCOD of the sludge, and showed the maximum increment at the SLR 8%. The SCOD of different SLR in raw sludge, after HTP and solubilization COD were shown in Fig. 2.

HTP as a pre-treatment technique could destroy the sludge floc structure and cell wall, improved the dissolution of organic matter in the sludge.[25] In this study, the solubilization COD were 95.41%, 96.09%, 94.78%, 89.67% and 62.96% for SLR 5%,
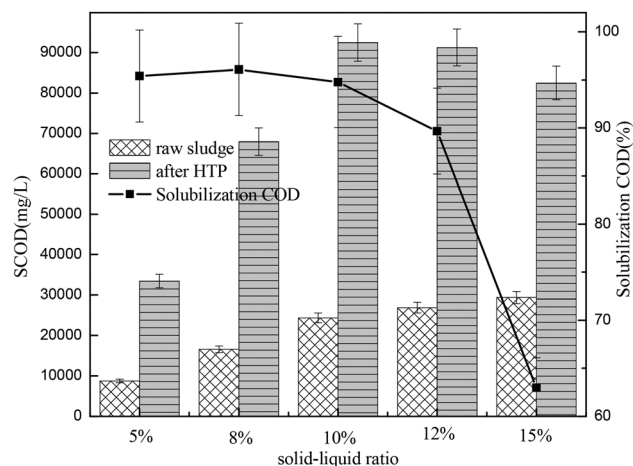
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Fig. 2 SCOD of different SLR raw sludge, after HTP and solubilization COD.

8%, 10%, 12% and 15%, respectively. From the SLR 8% to 15%, the solubilization COD were decreased as the SLR increased. Seong et al.[41] evaluated the COD solubilization for different TS concentrations under temperatures ranging from 100 to 220 °C. As TS concentration increased, the solubilization decreased gradually at 160 °C, which was consisted with our conclusion.

But when the SLR was 5%, the solubilization COD was lower than the SLR 8%. Viscosity was an important parameter which could affect the solubilization and biodegradability of sludge. The viscosity decreased with the SLR decreased.[42] On the other hand, when under the high temperature and pressure, the viscosity also decreased.[12] Therefore, the SLR 5%, led to more organic substances degraded or volatilized due to the lower viscosity, resulting in the decrease of the solubilization COD.

VS/TS were found to improve by 3.21%, 4.08, 2.10% and 1.89% for SLR 5%, 8%, 10% and 12% compared with the raw sludge, but the SLR 15% was further shown to decrease by 2.56%. It was probably that the organic matters including VS were pyrolyzed at 160 °C,[43] the more solid in sludge, the more escape of CO_2 for the organic compounds which reduced the volatile matters.

3.1.2 VFAs solubilization. In the process of anaerobic digestion, VFAs are important intermediate product of which methanogens mainly use to produce methane.[44] The concentrations of VFAs in the samples were shown in Table 2. Compared with the raw sludge, the concentrations of VFAs were improved by 49.81%, 58.78%, 26.92%, 38.44%, and 45.75% for SLR 5%, 8%, 10%, 12% and 15%, respectively. It could be observed that HTP had an important effect on VFAs production. During HTP, long chain fatty acids could be degraded to low chain fatty acids. Wilson reported that the amino acids decomposed to VFAs above 160 °C.[45] Moreover, the increment of VFAs were also influenced by the SLR, and the optimum SLR was 8%. It indicated that the low SLR were more effective at promoting the dissolution of long-chain organic acids. In addition, after HTP, the concentrations of acetic acids and butyric acids had a significantly increase compared with the raw sludge, since they were the degradation products of several

Table 2 Concentrations of the VFAs in the sludge after HTP

Parameter	5%		8%		10%		12%		15%	
	Raw	After HTP	Raw	After HTP	Raw	After HTP	Raw	After HTP	Raw	After HTP
Total VFAs (mg L^{-1})	159.58 ± 1.11	239.06 ± 0.99	235.66 ± 9.15	374.18 ± 8.09	297.72 ± 10.1	377.86 ± 1.44	333.02 ± 4.71	461.03 ± 1.68	369.12 ± 5.58	538.01 ± 5.18
Acetic acid (mg L^{-1})	34.75 ± 1.44	63.38 ± 1.44	36.77 ± 2.09	185.22 ± 6.76	38.79 ± 3.06	165.30 ± 5.1	58.44 ± 3.53	174.21 ± 4.68	78.70 ± 3.39	164.70 ± 4.86
Propionic acid (mg L^{-1})	69.72 ± 0.77	68.68 ± 0.9	72.55 ± 1.91	57.32 ± 1.48	72.23 ± 1.74	67.76 ± 1.27	74.55 ± 4.24	72.11 ± 1.68	82.02 ± 4.48	70.71 ± 4.78
Butyric acid (mg L^{-1})	55.11 ± 1.18	107.00 ± 1.63	126.34 ± 5.27	131.64 ± 2.3	186.70 ± 5.42	144.80 ± 1.19	200.03 ± 3.13	214.71 ± 4.91	208.40 ± 3.94	302.60 ± 5.76

organic matters. Li *et al.* also considered an increase of VFAs were due to the degradation of lipids.[46]

3.1.3 Nitrogen solubilization. Total nitrogen and ammonia nitrogen are important parameters, because they can inhibit the anaerobic digestion when above certain levels.[47] Table 3 showed the concentrations of TN and NH_4-N for different SLR of sludge.

After hydrothermal pretreatment (HTP), the NH_4-N solubilization were improved by 103.12%, 110.44%, 97.54%, 90.23%, and 101.37% for SLR 5%, 8%, 10%, 12% and 15%, respectively. Wilson and Novak[45] demonstrated that the proteins existing as particulate matter could be converted into NH_4^+-N through hydrothermal pretreatment, so the NH_4-N solubilization in all the samples increased. The trend of TN solubilization was similar to the NH_4-N. After HTP, the TN solubilization were improved by 102.16%, 107.54%, 60.04%, 77.43%, and 100.86% for SLR 5%, 8%, 10%, 12% and 15%, respectively. They both had the highest solubilization at the SLR 8%. It was probably because the lower SLR, the easier dissolution of nitrogen. In contrast, due to the minimum concentration of sludge for the SLR 5%, the nitrogen rapidly dissolved, and exposed under the high temperature and pressure for a longer time.[45] Hence, the NH_4-N and TN further volatilized and degraded.

3.2. Effect of HTP on different SLR sludge anaerobic digestion

3.2.1 Daily biogas production and methane content. The daily biogas production and methane content datas were presented in Fig. 3 and 4.

Fig. 3 showed the results of the daily biogas production in anaerobic digestion within 40 days. There were three remarkable peaks during anaerobic digestion for all the samples. The first peak of the daily biogas production were found to be 16.80, 42.50, 55.13, 22.27, 20.21 and 18.77 N ml g^{-1} VS for raw sludge, SLR 5%, 8%, 10%, 12% and 15%, respectively. For the different SLR, the first and second peak occurred earlier and the daily biogas production was higher compared with the raw sludge, which was due to the small particle size was benefit for degradation under the high temperature and pressure.[48] In contrast, the third peak was delayed compared with the raw sludge, it might be that the refractory organic matter had been effectively degraded for the raw sludge, but there were lots of refractory organic matter for the different SLR, thereby slow down the anaerobic digestion.

Following the BMP test, methane content was shown in Fig. 4. The methane content had a rising trend in the beginning, it was due to the decomposition of acetic acid.[49] The time reached on the first peak delayed for the raw sludge, it was because the refractory organic matter was difficult to dissolve, thus made the process slower than the others.[50] In the late stage of anaerobic digestion, the methane content was essentially stable in the range of 52-64%. It indicated that the composition of biogas contained around 50–70% methane, 20–30% carbon dioxide and less nitrogen and hydrogen sulphide gas.[51] Overall, after HTP, the methane contents were found to be higher than the raw sludge, which indicated that HTP had an effective effect on the sludge properties.[52] Also, the SLR 8% had the highest

Table 3 Concentrations of TN and NH_4–N in the sludge after HTP

| Parameters	5%		8%		10%		12%		15%	
	Raw	After HTP	Raw	After HTP	Raw	After HTP	Raw	After HTP	Raw	After HTP
TN (mg L^{-1})	784.5 ± 17.2	1996.4 ± 38.6	1132.4 ± 24.9	3400.8 ± 53.3	1459.1 ± 25.9	3263.1 ± 50.74	1654.3 ± 23.3	4054.6 ± 83.3	1894.1 ± 25.1	4072.7 ± 93.3
TNM (mg L^{-1})	1970.8 ± 33.4	3035.8 ± 50.7	3241.8 ± 58.9	4755.7 ± 52.0	4463.7 ± 69.7	5318.3 ± 70.7	4754.2 ± 79.2	6735.9 ± 97.3	4054.2 ± 62.8	7948.8 ± 107.3
NH_4-N (mg L^{-1})	579.2 ± 10.6	800.7 ± 10.6	817.8 ± 9.1	1326.2 ± 19.3	1048.8 ± 28.9	1580.0 ± 18.1	1206.4 ± 8.9	1680.6 ± 20.7	1383.0 ± 12.0	2174.0 ± 40.7
NH_4-NM (mg L^{-1})	794.0 ± 8.6	964.4 ± 9.7	1094 ± 13.5	2376.8 ± 39.3	1593.4 ± 18.5	2809.9 ± 30.5	1802 ± 14.7	3661.5 ± 28.4	2164 ± 14.8	4579.7 ± 67.2
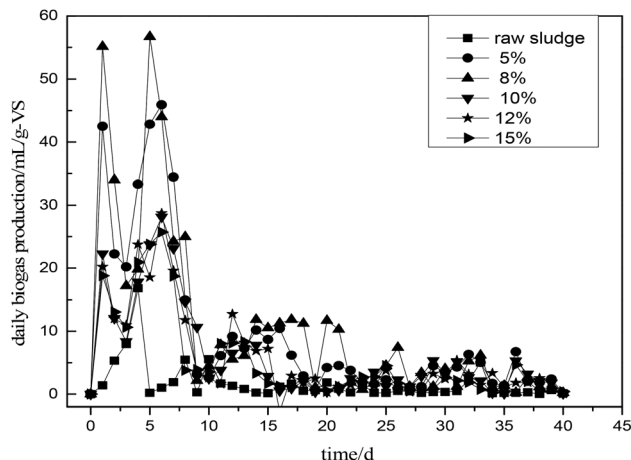
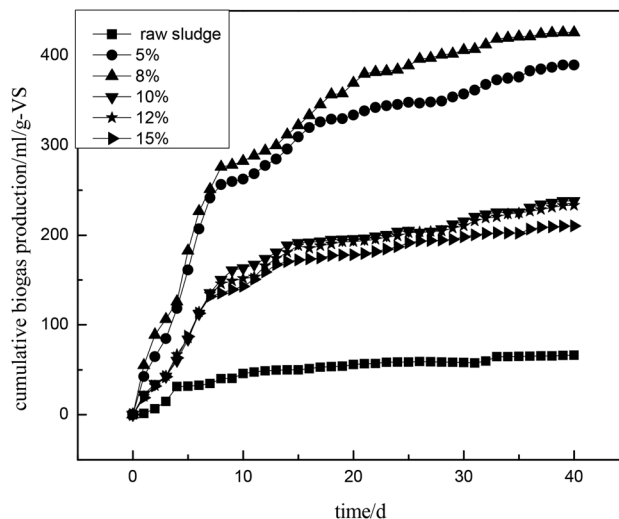Fig. 3 Change of daily biogas production.
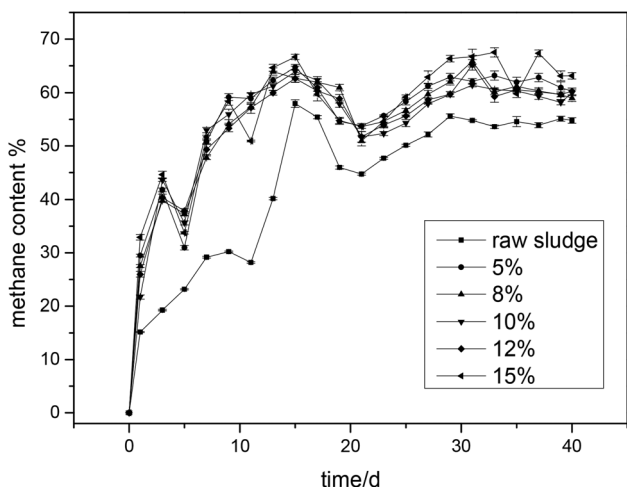

Fig. 5 Variation of cumulative biogas yield.

Fig. 4 Variation of methane content.

methane content, which was related to the VFAs production, seen in 3.1.2.

3.2.2 Cumulative biogas yield and T90. HTP led to the physical structure of sludge disrupt, thereby significantly enhanced the solubilization and biodegradation of sludge, improved anaerobic digestion.[13] Cumulative biogas yield was shown in Fig. 5. Based on the BMP tests, the cumulative biogas yield were 389.31, 425.57, 238.09, 233.20 and 210.48 N ml g^{-1} VS, for SLR 5%, 8%, 10%, 12% and 15%, respectively. Compared with the raw sludge (66.35 N ml g^{-1} VS), the cumulative biogas yield were increased by 486.7%, 541.4%, 258.8%, 251.4% and 217.2% for SLR 5%, 8%, 10%, 12% and 15%, respectively. It indicated that HTP had a positive effect on the biodegradation and hydrolysis of organic matters, led to the enhancement of biogas production.[33,53] Further more, the cumulative biogas yield increased gradually with the SLR decreased except for the SLR 5%. It was due to the cumulative biogas yield was corresponded with the solubilization COD, it could be improved as the solubilization COD increased, the tendency was consistent with the 3.1.1. Considering biogas production capacity and

efficiency, the SLR 8% was suggested as a preferable condition on anaerobic digestion.

T90 is the time taken for 90% biogas production, and also is an important index in practical engineering.[54] The datas were shown in Table 4. After HTP, the T90 were earlier 3, 9, 2, 2, and 7 days for SLR 5%, 8%, 10%, 12% and 15%, respectively, than the raw sludge, and over 85–90% of cumulative biogas production was obtained between 20 to 30 days. It can be observed that the SLR 8% had the lowest T90.

3.3. Kinetic analysis

3.3.1 Modified Gompertz model. The cumulative biogas production obtained from BMP tests were fitted with the modified Gompertz model. The kinetic parameters estimated from the modified Gompertz equation were given in Table 5. It could be observed the cumulative biogas production, max biogas potential, max biogas production rate and lag time. The maximum biogas potential were found to be 360.81, 403.79, 217.07, 213.87, 196.52 and 61.66 N ml g^{-1} VS for SLR 5%, 8%, 10%, 12%, 15% and raw sludge, respectively. The results showed that due to the high biodegradation of the substrate, HTP significantly improved the maximum biogas potential. The SLR 8% had the highest maximum biogas potential yield because it had the maximum dissolution of organic matter. On the other hand, the lag time was not obvious, the time was

Table 4 T90 of different SLR after HTP

Parameter	T90 (d)	25d cumulative biogas production (N ml g^{-1} VS)
Raw sludge	32	58.46
SLR 5% after HTP	29	344.14
SLR 8% after HTP	23	382.45
SLR 10% after HTP	30	200.47
SLR 12% after HTP	30	197.76
SLR 15% after HTP	25	184.36

Table 5 Model parameters of kinetic study

Parameter	Modified Gompertz model					
	Raw	5%	8%	10%	12%	15%
Cumulative biogas production-experimental (N ml g^{-1} VS)	66.35	389.31	425.58	238.09	233.20	210.48
Cumulative biogas production-predicted (N ml g^{-1} VS)	61.63	360.67	403.47	216.97	213.74	196.45
Max biogas potential (N ml g^{-1} VS)	61.66	360.81	403.79	217.07	213.87	196.52
R_m (ml d^{-1} g^{-1} VS)	4.81	29.39	30.24	17.34	16.43	16.24
Lag time (λ)	2.21×10^{-16}	1.79×10^{-15}	0	0.0073	7.23×10^{-19}	5.29×10^{-15}
R^2	0.9524	0.9700	0.9654	0.9695	0.9700	0.9753
RMSE	3.84	17.48	21.36	11.01	10.62	8.76
FPE	0.0033	0.0020	0.0025	0.0021	0.0021	0.0017

calculated between 0 to 0.0073 days. It indicated that the anaerobic digestion started quickly. Also, the raw sludge had the lowest value of R^2 (0.9524) and the maximum value of FPE (0.0033). It indicated that the raw sludge had the highest roughness of the cumulative biogas production. While the SLR 15% had the highest R^2 (0.9753) and the lowest FPE (0.0017). It revealed that the SLR 15% had a better fit with the modified Gompertz model.

Fig. 6(a) showed the results of Cumulative biogas production-experimental and modified Gompertz model. The results demonstrated the feasibility of applying the modified Gompertz model to develop the kinetic model of cumulative biogas production due to the high correlation coefficient (R^2 = 0.97524–0.9753), and low FPE (0.0017–0.0033) and RMSE (3.84–21.36), indicated a strong linear relationship between the experimental data and the model. Several researchers had used the modified Gompertz model to evaluate the biogas production in the process of anaerobic digestion and had a good fit with the results. Syaichurrozi et al.[55] researched the kinetic of biogas production and obtained the R^2 values between 0.958 to 0.969, and the lag time was between 0.213 to 0.345 days. Cheong et al.[56] studied the anaerobic hydrogen production of the cattle manure sludge and discussed the kinetic study of the modified Gompertz model, the R^2 values they obtained were between 0.997 to 1.000, and the RMSE were between 0.16 to 7.06.

The comparison between the predicted and experimental cumulative biogas production values for the six samples were shown in Fig. 6(b). It showed that the R^2 value was obtained as 0.9662 when used the modified Gompertz model. The overall percentage deviation for the six samples was +26.7%. The results indicated that the experimental data could be fitted with the modified Gompertz model and could used the model to determine the cumulative biogas production, max biogas potential, maximum biogas production rate and lag time.

3.3.2 Logistic model. Table 6 showed the kinetic parameters calculated from the Logistic equation. The lag time was between 1.20×10^{-15} to 4.65 days, which was higher than the results of the modified Gompertz model. The correlation coefficient (R^2) values for the six samples (SLR 5%, 8%, 10%, 12%, 15% and raw sludge) were 0.9533, 0.9461, 0.9571, 0.9548, 0.9607 and 0.9297, respectively. The correlation coefficient (R^2) values showed that the experimental results could be fitted with the

Logistic model. And the SLR 15% had the highest R^2 (0.9607), but the raw sludge had the lowest R^2 (0.9297). This results were similar with the modified Gompertz model. Adjusting the SLR
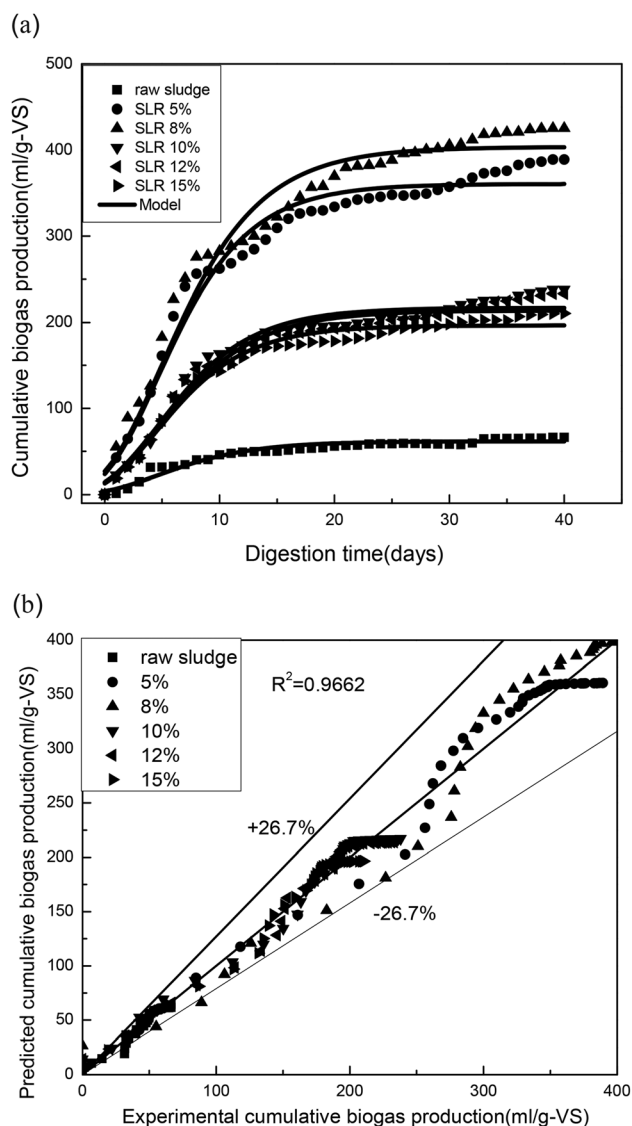

(a)

(b)

Fig. 6 (a) Cumulative biogas production-experimental and modified Gompertz model. (b) Comparison between experimental and predicted (modified Gompertz model) cumulative biogas production.

Table 6 Model parameters of kinetic study

	Logistic model					
Parameter	Raw	5%	8%	10%	12%	15%
Cumulative biogas production-experimental (N ml g^{-1} VS)	66.35	389.31	425.58	238.09	233.20	210.48
Cumulative biogas production-predicted (N ml g^{-1} VS)	59.88	356.33	399.05	213.51	210.79	193.99
Max biogas potential (N ml g^{-1} VS)	59.88	356.34	399.08	213.52	210.80	193.99
R_{m} (ml d^{-1} g^{-1} VS)	4.67	28.05	28.53	17.31	15.75	15.57
Lag time (λ)	2.87×10^{-15}	1.75×10^{-15}	2.67	0.23	4.65	1.20×10^{-15}
R^2	0.9297	0.9533	0.9461	0.9571	0.9548	0.9607
RMSE	4.58	21.81	26.14	13.16	13.13	11.13
FPE	0.0048	0.0031	0.0038	0.0031	0.0032	0.0028

of sludge was benefit to improve the cumulative biogas production. Also, the raw sludge had the highest value of FPE (0.0048) and the SLR 15% had the lowest value of FPE (0.0028).

(a)

(b)

Fig. 7 (a) Cumulative biogas production-experimental and Logistic model. (b) Comparison between experimental and predicted (Logistic model) cumulative biogas production.

Therefore, the Logistic model could accurately reflected the cumulative biogas production of anaerobic digestion, and the SLR 15% had a better fit with the Logistic model. The fitted curves for Logistic model were shown in Fig. 7(a), it evaluated the model results for the Logistic model, there were not much difference of the cumulative biogas production between the experimental values and model datas.

Fig. 7(a) showed the comparison of predicted and experimental cumulative biogas production values for the six samples. The R^2 value was obtained as 0.9436 when used the Logistic model. The overall percentage deviation for the six samples was +32%. This showed that the experimental data could be fitted with the Logistic model for kinetic study and the Logistic model could determined the cumulative biogas production, max biogas potential, max biogas production rate and lag time accurately.

It could be observed that the correlation coefficient (R^2) values of the Logistic model were lower than the modified Gompertz model. Root mean square error (RMSE), Final Prediction Error (FPE) and overall percentage deviation of the Logistic model were higher than the modified Gompertz model. This indicated that the modified Gompertz model fitted well for the kinetic study of anaerobic digestion process. So the modified Gompertz model was more suitable for the evaluation of anaerobic digestion kinetic study.

4. Conclusions

In this study, the solubilization COD, NH$_4$-N, VFAs, biogas production for the different SLR between the raw sludge and after HTP were analysed. HTP had promoting effect on anaerobic digestion, which increased the solubilization of organic matter. However, the different SLR had an important influence on anaerobic digestion. The results showed that the SLR 8% was conducive to the solubilization of COD, also had the highest cumulative biogas yield and methane content. The solubilization COD reached at 96.09%, the cumulative biogas yield was 425.57 N ml g^{-1} VS, and the methane content reached on 67%. Therefore, controlling the SLR of sludge in the suitable range would benefit to the dissolution of organic matter. It could not only saved the cost of sludge treatment, but also improved the methane content. The modified Gompertz model and Logistic
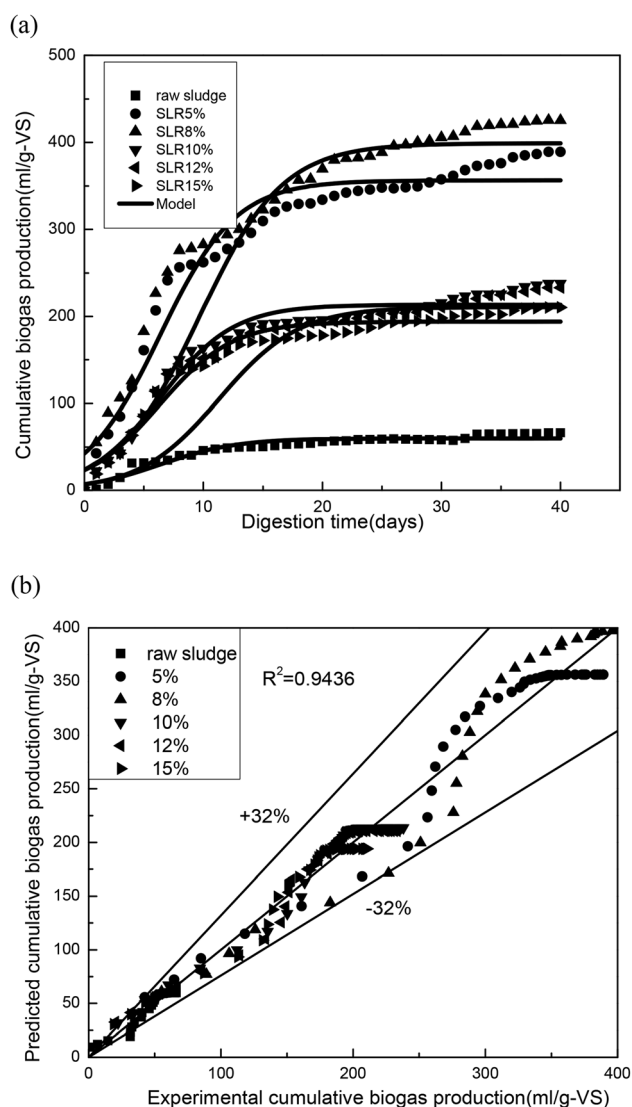
model were used to evaluate the performance of anaerobic digestion, and two models had a good fit. The higher values of the R^2 were between 0.97524 to 0.975, the lower values of the FPE were between 0.0017 to 0.0033 and the RMSE were between 3.84 to 21.36. It demonstrated that the modified Gompertz model was better fitted with the experimental datas than the Logistic model. Finally, the methane production at suitable range of SLR increased significantly, which provided the basis for the industrial application.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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