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Effect of substrate feeding strategy of a semi-pilot-scale single-stage reactor under different hydraulic retention time and multiple kinetic models analysis

Sagor Kumar Pramanik[a], Fatihah Binti Suja[a,*], Biplob Kumar Pramanik[b]

[a]*Department of Civil and Structural Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia; 43600 UKM Bangi Selangor, Malaysia, Tel. +601 9304 2621; emails: fati@ukm.edu.my (F.B. Suja), sagorpramanik02@gmail.com (S.K. Pramanik)*
[b]*School of Engineering, RMIT University, Melbourne, VIC 3000, Australia, email: biplob.pramanik@rmit.edu.au (B.K. Pramanik)*

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ABSTRACT

The improper management and uncontrolled discharge of huge amounts of food waste have been creating environmental pollution and sanitation-related problems. Anaerobic digestion is considered the most attractive and widely applied technique for the treatment of food waste. This study investigated the effect of feeding mode on the performance of a semi-pilot (160 L) single-stage reactor under different hydraulic retention time (HRT). The reactor was operated under two different feeding modes: daily feeding and feeding 3-times-per-week. Daily feeding mode displayed more stable and efficient performance than feeding mode 3-times-per-week. The maximum biogas yield (1.01 L/g VS_{added}) and maximum methane yield (0.71 L/g VS_{added}) in the daily feeding mode at an HRT of 124 ds was higher than that of the feeding mode 3-times-per-week by 11% and 15%, respectively. The accumulation of volatile fatty acid was noticed in both feeding modes, but the accumulation of ammonia was only found in the feeding mode 3-times-per-week. Higher removals of volatile solid (VS) (92.7%) and chemical oxygen demand (COD) (95.84%) were observed for the daily feeding mode at an HRT of 124 ds compared to the feeding mode 3-times-per-week. The removal efficiency of VS and COD during the daily feeding mode increased by 8% and 10%, respectively, compared to the feeding mode 3-times-per-week. Four kinetic models—a first-order-kinetic model, a modified Gompertz model, a logistic function model, and a Cone model—were used to fit the cumulative methane production obtained from the experimental data. The kinetic study indicated that the modified Gompertz model had the best fit (R^2 = 0.994–0.998) with the experimental data for both feeding modes.

Keywords: Daily feeding mode; 3-times-per-week feeding mode; Food waste; Anaerobic digestion; Hydraulic retention time; Biogas; Methane; Kinetic study

1. Introduction

In recent years, the increasing quantity of food waste has become a serious issue contributing to adverse environmental and sanitation challenges all over the world. Food is wasted throughout the food supply chain, and the causes of food waste generation in different countries are mainly connected to economic conditions, socio-cultural factors and inadequate waste management infrastructure [1,2]. Kasavan et al. [1] reported that food wastage at the retail and consumer stages is significantly more in the United States, whereas higher food wastage was seen in the food production and immediate post-harvest stages in Southeast Asia due to a lack of technology, transportation and storage facilities. Pramanik et al. [3] pointed out that Malaysia disposed of 16,687 tons of food waste in landfills daily, with the food waste comprising almost 55% of municipal solid waste. In Malaysia, the majority of waste (85%) is collected

* Corresponding author.

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and sent to landfills, since the landfill disposal process is comparatively cheap and simpler to utilize compared to other methods [4]. Malaysia has 170 operating waste disposal sites, among which only 14 have been classified as sanitary. On the other hand, the disposal of raw organic waste in landfills has been banned in Sweden and Germany, as landfill disposal causes severe environmental problems including toxic gas emissions, groundwater contamination, leachate generation, and offensive odors [5]. When food waste decomposes in landfills, it releases CH_4, an extremely powerful greenhouse gas that traps 21 times more heat than CO_2 [1]. In Malaysia, there are already advanced incineration technology available to dispose of toxic wastes, with seven mini incinerators operating in select islands, namely Pangkor, Langkawi, Labuan, and Tioman [6]. However, the energy recovery from incineration is not economically feasible because the high moisture content of food waste results in a low heating value [5,7]. Neither landfill nor incineration is suitable for the management of food waste. Other methods should be used to recover sustainable energy from food waste. Thus, there is an inevitable need to look for eco-friendly and economical alternatives to landfills and incineration.

Anaerobic digestion is a widely practiced green technology. It is considered to be one of the most suitable techniques for food waste treatment because of its good environmental impact and good energy recovery that can be achieved from methane production [8,9]. Nutrient-rich sludge residue (digestate) obtained from the anaerobic digestion process can be recycled into organic fertilizer [10]. The performance of anaerobic digestion is dependent on several factors such as feeding mode, reactor design, hydraulic retention time (HRT), organic loading rate (OLR), pH, and temperature [11]. Many studies have explored the anaerobic digestion process and control parameters (such as pH, volatile fatty acid (VFA), ammonia, total alkalinity (TA), biogas production, and methane content) to improve the anaerobic digestion process stability and efficiency [8,12–18]. However, most studies have only focused on anaerobic digestion performance monitoring under certain operational states of the digester. Researchers have also tried to compare the single-stage reactor with the multistage reactor and mesophilic conditions vs. thermophilic conditions under elevated OLRs (or decreased HRTs) [19–27]. In recent times, several researchers indicated that feeding mode impacts biogas production in anaerobic reactors, but results are conflicting [28–33]. Some studies reported that daily feeding regimes displayed better performance compared with the continuous/stepwise feeding modes, whereas other studies led to the opposite conclusion. Most studies in the past have used either fiber-based substrates [30–32], acetate [33], or wastewater [29]. Therefore, research on how feeding mode affects food waste anaerobic digestion is lacking. Furthermore, most of these studies have been carried out with laboratory-scale reactors (a maximum volume of almost 15 L). The physical characteristics of semi-pilot-scale anaerobic reactors (volume, stirring speed, and feeding mode) usually differ from that of laboratory-scale anaerobic reactors [28]. Hence, this paper investigates the effect of feeding mode on the performance of a semi-pilot-scale anaerobic reactor to address the gap in this field.

The anaerobic digestion of food waste is a complex biological process that involves a series of biochemical reactions carried out by different groups of microorganisms, so active monitoring is required for the stable operation of anaerobic digestion [34]. During hydrolysis, the complex structure of food waste is solubilized, after which volatile organic acid is produced in the acidogenesis stage. Then, acetate, hydrogen, and carbon dioxide are generated and oxidized during the acetogenesis stage. Finally, methane is produced during the methanogenesis stage [34,35]. Svensson et al. [28] reported that the above-mentioned product concentrations fluctuate when feeding reactors once per day. Additionally, variations in product concentrations affect process thermodynamics and alter the ecosystem to select new bacterial community. Hence, it was anticipated that feeding mode will affect the performance of anaerobic reactors fed with food waste.

The knowledge of digestion kinetics is significant for predicting anaerobic digestion performance, optimizing the anaerobic digestion process, and designing reactors [36,37]. Bala et al. [38] reported that a kinetic study is essential for predicting the impact of substrate concentration and composition, dilution rate, and temperature. A kinetic study can not only be used to compare the methane production rate of different substrates, but also to understand the impacts of changing the process parameters on anaerobic digestion performance [38,39]. Zhang et al. [37] pointed out that the parameters of various kinetic models offer a better understanding of the biological reaction mechanism in the anaerobic digestion process, which in turn, assist researchers to achieve the required simulated outcomes by reducing the time required for performing experiments. Various kinetic models have been applied to analyze lag phase, hydrolysis rate, and methane production rate and to predict methane yield. For example, Deepanraj et al. [35] studied the anaerobic digestion kinetics of food waste using a modified Gompertz model and a logistics model in laboratory-scale reactors operating in batch mode. The modified Gompertz model and the first-order-kinetic model were also used in another study to determine the kinetics of food waste anaerobic digestion in batch laboratory-scale reactors [36]. Li et al. [40] applied five kinetic models—the Cone model, the modified Gompertz model, the first-order model, the transference function model, and the Fitzhugh model—to define the anaerobic digestion kinetics of food waste in batch laboratory-scale reactors. However, the kinetic modeling of food waste anaerobic digestion under different feeding modes has not yet been fully explored.

Based on the identified gaps in the current literature, this study aims to investigate the effect of feeding mode on the performance of a semi-pilot (160 L) anaerobic single-stage reactor operated under mesophilic conditions. The results of biogas production, ammonia concentration, VFA, and TA concentration, as well as organic removal efficiency (such as VS and chemical oxygen demand (COD)) under different HRTs were compared and discussed. Four kinetic models (i.e., first-order-kinetic model, Cone model, modified Gompertz model, and logistic function model) were used to describe the kinetics and mechanisms of anaerobic digestion. A comparative assessment of the four kinetic models was carried out to estimate the most appropriate model to accurately predict methane production.

2. Materials and methods

2.1. Substrate and inoculum

Food waste was used as a substrate and collected from a cafeteria near the Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Malaysia. The food waste consisted of rice, vegetables, noodles, pasta, fruits, bread, egg, meat, and fish. Different impurities such as plastic, metal, eggshells, bags, tissue, and other non-biodegradable materials were manually removed from the food waste. The food waste was then mixed with a kitchen blender and filtered through a USA standard no. 16 sieve (nominal diameter = 1.0 mm) to ensure uniformity. The basic characteristics of the food waste used in this experiment are listed in Table 1. Fresh cow manure (CM) and mesophilic anaerobic sludge were used as an inoculum in this study. Approximately 35 kg of fresh CM was collected from a local farm near Bangi, Malaysia. Almost 65 L of anaerobic sludge was collected from a semi-pilot scale anaerobic reactor operated under mesophilic conditions. For the feeding mode 3-times-per-week, fresh CM was mixed manually with tap water until the volume of the slurry reached 124 L. For the daily feeding mode, fresh CM, and mesophilic anaerobic sludge were manually mixed with tap water until the volume of the slurry reached 124 L. Prior to use, the inoculum was passed through a 1 mm sieve to remove any larger particles or grit. The characteristics of the inoculum used in this experiment are shown in Table 1. Both the food waste and the inoculum were stored at 4°C in an airtight plastic container to prevent any degradation until their next use.

2.2. Experimental design

A single-stage semi-pilot high-density polyethylene (HDPE) anaerobic reactor (160 L) was operated with a working volume of 124 and 36 L headspace. This system was located in an open environment, with full exposure to Malaysia's hot and humid weather throughout the year. The reactor was equipped with a stainless-steel stirrer with four arms to provide sufficient mixing of substrates; performed manually 3 times a day for 10 min. The length and thickness of the arms of the stirrer were 30 and 10 cm, respectively. The speed of the arms of the stirrer was 40 rpm. Before removal of the digestate, the speed was increased to 70 rpm to ensure homogeneity in the reactor. For biofilm attachment, the reactors were filled with 9,000 units of K-1 HDPE media measuring 1.6 cm in diameter and 1 cm thick, bought from amazon.com. The outlets of the reactors were installed with stainless-steel sieves with an opening diameter of 0.6 cm, to ensure that the plastic media remained inside the digester.

Table 1
Characteristics of the food waste and inoculum used in this study

Parameter	Unit	Inoculum	Daily feeding mode	3-times-per-week feeding mode	
			Stage 1–4	Stage 1	Stage 2 and 3
TS	g/L	32.64 ± 0.19	65 ± 0.15	66 ± 2.41	96.42 ± 0.62
VS	g/L	19.58 ± 0.31	62 ± 0.28	63 ± 2.27	92 ± 0.62
VS/TS ratio		0.60	0.95	0.96	0.95
pH		7.57 ± 0.15	4.52 ± 0.18	4.91 ± 0.16	4.57 ± 0.28
tCOD	g/L	27.3 ± 1.84	108.1 ± 1.5	110 ± 8.16	160.9 ± 1.13
sCOD	g/L	7.5 ± 0.42	30.65 ± 1.38	35 ± 3.8	51.6 ± 1.64
NH_3–N	g/L	3.36 ± 11.43	0.98 ± 5.89	1.04 ± 6.52	1.13 ± 7.52
TKN	g/L	5.32 ± 16.78	3.5 ± 15.3	3.56 ± 10.7	3.78 ± 12.58
VFA	g HOAc/L	1.13 ± 57.98	3.13 ± 106.1	3.59 ± 99.6	4.57 ± 144.91
TA	g $CaCO_3$/L	5.15 ± 253.2	–	–	–
VFA/TA		0.21	–	–	–
Moisture content	%	96.5 ± 0.31	93.8 ± 0.22	93.2 ± 0.16	90.3 ± 0.19
Ash	%	0.6 ± 0.32	1.1 ± 0.12	1.3 ± 0.15	1.6 ± 0.13
[a]Protein	%	1.3 ± 1.46	1.7 ± 5.21	1.6 ± 7.24	1.8 ± 10.35
Total fat	%	0.29 ± 2.45	1.1 ± 9.35	1.4 ± 8.75	2.1 ± 12.54
[b]Total carbohydrate	%	0.9 ± 5.76	2.6 ± 12.96	2.5 ± 13.54	3.4 ± 11.78
C	%	35.21 ± 3.61	46.09 ± 0.41	47.69 ± 0.04	53.01 ± 0.3
H	%	4.7 ± 0.25	6.94 ± 0.05	7.38 ± 0.01	8.25 ± 0.34
N	%	2.86 ± 0.73	3.19 ± 0.04	3.20 ± 0.12	5.43 ±
S	%	0.07 ± 0.001	0.203 ± 0.02	0.245 ± 0.01	0.3 ± 0.15
C/N		10.98	14.42	14.95	9.77

TS: total solid; VS: volatile solid; tCOD: total chemical oxygen demand; sCOD: soluble chemical oxygen demand; NH_3–N: ammonia–nitrogen; TKN: total Kjeldahl nitrogen; VFA: volatile fatty acid; TA: total alkalinity; C: carbon; H: hydrogen; N: nitrogen; S: sulfur.
[a]Protein content was calculated by multiplying the organic nitrogen value (TKN subtracted by NH_3–N) by 6.25.
[b]Total carbohydrate = 100 – (Ash + moisture + fat + protein).

The reactors were operated under mesophilic conditions and the operational temperature was varied between 30°C and 34°C. No external heat exchangers were used to maintain the reactor temperature because Malaysia is already characterized by hot and humid weather throughout the year.

2.3. Operation and monitoring of the reactor

The reactor was operated in two phases for a total of 255 d. In the first phase, the reactor was operated over 78 d, defined as the 3-times-per-week feeding mode. In the second phase, the reactor was run over 178 d, that is, the daily feeding mode. In the beginning, reactor was inoculated with 124 L of the CM slurry and mesophilic anaerobic sludge. After that, the reactor start-up was commenced by acclimatizing the environment in the reactor using synthetic wastewater according to the composition shown in Table 2. This synthetic wastewater contains all components necessary to ensure the stable operation of the microbial community during the anaerobic digestion process. The start-up operation of the reactor was executed for 2 weeks with synthetic 260 mL wastewater a day and an OLR of 0.01 kg COD/m^3/d. This low-strength synthetic wastewater was used to provide low organic stress to the reactors.

After a successful start-up, the reactor was operated under different successive operational stages in reference to a sequence of decreasing HRTs of 124, 62, 41, and 31 d for the daily feeding mode. On the other hand, the reactor was operated under a sequence of decreasing HRTs of 124, 62, and 35 d for the feeding mode 3-times-per-week. During the daily feeding mode, food waste was fed once a day throughout operations at varying HRTs by adjusting the feeding rates. The VS concentration of the daily feeding mode was kept constant (62 g/L) during operation. Therefore, as the HRT was decreased, the OLR also increased. In contrast, for the feeding mode 3-times-per-week, food waste was fed 3 times a week (i.e., Saturday, Tuesday, and Thursday) at varying HRTs by adjusting the feeding rates. The VS concentration of the feeding mode 3-times-per-week was 62 g/L at an HRT of 124 d. However, the VS concentration was increased from 62 to 95 g/L at an HRT of 62 and 35 d during the feeding mode 3-times-per-week. The operational conditions of the reactor are shown in Table 3.

Sampling of the reactor was performed every 24 h and 3-times-per-week immediately before feeding during the daily and 3-times-per-week feeding mode, respectively. Sampling was performed using a sampling pipe to measure several parameters including the pH, temperature, VFA, total alkalinity (TA), and ammonia nitrogen (NH_3–N) for monitoring purposes. The effluent from the reactor was used to check the digester's performance and organic removal efficiency throughout its operation. The collected effluents were first stirred to achieve homogeneity and then placed into an HDPE bottle and sampled. The samples were stored following EPA guidelines [41] until removal for testing. The biogas component (e.g., methane (CH_4) and carbon dioxide (CO_2)) and biogas volume were measured on-site using a portable biogas analyzer and supel™-inert multi-layer foil gas sampling bags, respectively.

2.4. Analytical methods

A few methodologies were used to determine the total and soluble parameters. The pH and temperature were measured using test probes. The total solids (TS), VS, NH_3–N, and total Kjeldahl nitrogen (TKN) were measured using the Standard Method for the examination of water and wastewater [42]. For the assessment of VFA, TA, and soluble COD (sCOD), the samples were first filtered using a 0.45 μm cellulose nitrate filter paper before subsequent testing. VFA and TA were analyzed according to the esterification method (Method 8196, DR 6000 spectrophotometer-HACH, USA) and digital titrator method (Method 8203-HACH, USA), respectively. The reactor's digestion method (COD High Range, DR 6000 spectrophotometer-HACH, USA) was used to determine the concentration of total COD (tCOD) and sCOD. The elemental composition (Carbon (C), Hydrogen (H), Nitrogen (N), and Sulfur (S)) of the sample was determined using a CHNS 628 Series elemental analyzer (Leco corporation, USA). The CHN and S concentration were determined by subjecting the reaction to complete combustion at 950°C and 1,350°C, respectively. According to

Table 2
Composition of the synthetic wastewater

Name of Chemicals	Unit	Quantity
Glucose	mg	5,300
Beef extract	mg	840
$CaCl_2·2H_2O$	mg	61.2
$MgSO_4·7H_2O$	mg	64.3
NH_4Cl	mg	333.3
Distilled water	–	Full to 1 L

Table 3
Operational conditions of the single-stage anaerobic reactor

Stage	Daily feeding mode				3-times-per-week feeding mode		
	1	2	3	4	1	2	3
Duration (days)	0–65	66–118	119–148	149–178	0–37	38–63	64–77
Q (L/d)	1	2	3	4	1	2	3.5
OLR (kg VS/m^3/d)^3	0.5	1	1.5	2	0.51	1.4	2.45
HRT (d)	124	62	41	31	124	62	35

Q: influent flow rate; HRT: hydraulic retention time; OLR: organic loading rate.

the methods described by Association of Official Analytical Chemists (AOAC) [43], total fat was measured in a Soxhlet system by extraction with petroleum ether solvent, and protein content was calculated by multiplying with 6.25. Meanwhile, ash content was determined by incinerating the samples at 550°C in a muffle furnace and moisture content was measured by drying well-ground samples at 103°C–105°C in an oven at a constant weight. All laboratory analyses were performed at a room temperature of 22°C ± 2°C and in duplicates. Biogas was collected in gas collection bags (supel™-inert multi-layer foil bag), whereas the methane and carbon dioxide content in the biogas was measured using a gas analyzer (Biogas 5000, Geotech, UK).

2.5. Kinetics study and statistical analysis

Four kinetic models, namely a first-order-kinetic model (Eq. (1)), a modified Gompertz model (Eq. (2)), a Cone model (Eq. (3)), and a logistic function model (Eq. (4)) were used to fit the cumulative methane production obtained from the experimental data. These four models were chosen since many studies have used them frequently in the last few years to characterize and predict the kinetics of methane production in the anaerobic digestion process [35–40,44]. The first-order-kinetic model provides knowledge of the anaerobic degradation of food waste, wherein the hydrolysis becomes the rate-limiting step that controls the whole process [44]. This model, however, does not predict the conditions for lag phase, maximum biological activity, or process failure [45]. Meanwhile, the modified Gompertz model is an empirical non-linear regression model that characterizes cell density during microbial growth phases such as exponential growth rates and lag phase duration [45,46]. This model considers the duration of the lag phase as a crucial feature that governs methane production [38]. The Cone model is an empirical model that can describe the behavior of methane production using a shape factor, therefore indicating whether or not there is a lag phase in the digesters [37]. The logistic function model is based on the assumption that methane production rate is proportional to the volume of methane already produced, the highest capacity of methane production, and the highest methane production rate [44]. The logistic function correlates with the global profile of methane production kinetics, that is, with early exponential growth and the final stabilization at the maximum production level. Therefore, all four kinetic models were used in this study to analyze the lag phase duration, hydrolysis kinetics, and highest methane production of the reactor. These models operate based on Eqs. (1)–(4):

$$\text{First order kinetic model}: M = P_b \times \left[1 - \exp(-kt)\right] \quad (1)$$

$$\text{Modified Gompertz model}:$$
$$M = P_b \times \exp\left\{-\exp\left[\frac{R_m \cdot e}{P_b}(\lambda - t) + 1\right]\right\} \quad (2)$$

$$\text{Cone model}: M = \frac{P_b}{(1+kt)^{-n}} \quad (3)$$

$$\text{Logistic function model}: M = \frac{P_b}{1 + \exp\left\{\frac{4.R_m \cdot (\lambda - t)}{P_b} + 2\right\}} \quad (4)$$

where M is the methane yield (L/g VS_{added}) with respect to time t (d); P_b is the maximum methane potential of the substrate (L/g VS_{added}); k is the hydrolysis rate constant (1/d); t is the digestion time (d); R_m is the maximum methane production rate (L/g VS_{added} d); λ is the lag phase time (d); e is the Euler's function equal to 2.7183; n is the shape factor.

A nonlinear least-square regression analysis was performed using SPSS software (IBM SPSS statistics 25) to determine K, R_m, λ, and predicted methane yield. The coefficient of determination (R^2) and the root mean square error (RMSE) of each model were calculated to compare the accuracy of the studied models. The R^2-value is also known as the goodness-of-fit-index, which was determined using SPSS 25 software. RMSE, given by Eq. (5), is interpreted as the standard deviation between the predicted values and the measured values, with a lower RMSE indicating a better fit [36].

$$\text{RMSE} = \sqrt{\sum_{i=1}^{n} \frac{(\text{PV}_i - \text{MV}_i)^2}{n}} \quad (5)$$

where PV_i is the predicted methane volume, MV_i is the measured methane volume, and n is the number of measurements.

The second-order Akaike information criterion (AIC) (Eqs. (6) and (7)) and the Bayesian information criterion (BIC) (Eq. (8)) tests were used to compare the models and to determine the model that will more likely be correct [39]. The equations for these tests are:

$$\text{AIC} = N \ln\left(\frac{\text{RSS}}{N}\right) + 2K + \frac{2K(K+1)}{(N-K-1)}, \quad \text{when } \frac{N}{K} < 40 \quad (6)$$

$$\text{AIC} = N \ln\left(\frac{RSS}{N}\right) + 2K, \quad \text{when } \frac{N}{K} \geq 40 \quad (7)$$

$$\text{BIC} = N \ln\left(\frac{\text{RSS}}{N}\right) + K \ln(N) \quad (8)$$

where N is the number of data points, K is the number of parameters fit by the regression model, and RSS is the residual sum of squares.

3. Results and discussion

3.1. Characteristics of food waste

Food waste obtained from a cafeteria near Universiti Kebangsaan Malaysia was characterized and the value of most of the measured parameters displayed in Table 1. The food waste comprised rice, vegetables, noodles, pasta, fruits, bread, egg, meat, and fish. Pramanik et al. [2] reported that the characteristics of food waste changes according to consumption pattern, geographical change, seasonal change, and cooking procedure. According to Table 1, the total solid (TS) and volatile solid (VS) content of food waste ranged from 65 to 96.42 and 62 to 92 g/L, respectively, while the moisture content in the food waste ranged from 90.3% to 96.5%. Zhang et al. [47] pointed out that food waste is an easily biodegradable organic substrate due to its high moisture content. However, the food waste used in this study had an especially high organic content, with a VFA value of (3,125–4,573) mg HOAc/L, making its pH consistently low (pH 4.5–pH 4.91), all throughout the operation (Table 1). Due to its excellent biodegradability and high organic content, food waste was considered a suitable substrate that can be treated via anaerobic digestion.

The characteristics of food waste also define the relative quantities of organic carbon (C) and nitrogen (N) present in the food waste, whereas the C/N ratio of food waste ranged from 9.77 to 14.95. As shown in Table 1, the total carbohydrates, proteins, and fats in the food waste ranged from 2.6% to 3.4%, 1.4% to 2.6%, and 1.1% to 2.1%, respectively (Table 1). Carbohydrate-rich and protein-rich food waste have a higher hydrolysis rate because of their rapid degradability compared to lipid-rich food waste that can produce high methane yields [2]. It was reported that food waste rich in carbohydrate resulted in imbalanced C/N ratios because of nutrient limitations and quick acidification, while food waste rich in protein caused ammonia to accumulate. A lower nitrogen concentration in food waste means that the nitrogen is not the rate-limiting factor in the system. However, the ammonia concentration should be monitored throughout the operation to ensure that the accumulation of ammonia does not surpass the recommended threshold toxicity value (>3 g/L) [48].

3.2. Effect of feeding mode on biogas production at different HRTs

Figs. 1 and 2 show the biogas yield in daily feeding mode and feeding mode 3-times-per-week, respectively, at different HRTs during the anaerobic digestion of food waste. It was found that the biogas production in both feeding mode started immediately on the 1st day of digestion. When the HRT was decreased from 124 to 31 d, the biogas yield in both feeding modes decreased concurrently. The average biogas yields in daily feeding mode were 0.79 ± 0.17 L/g VS_{added} at 124 d HRT, 0.68 ± 0.13 L/g VS_{added} at 62 d HRT, 0.26 ± 0.09 L/g VS_{added} at 41 d HRT, and 0.08 ± 0.04 L/g VS_{added} at 31 d HRT (refer to Table 4). On the other hand, the average biogas yields in feeding mode 3-times-per-week were 0.59 ± 0.24, 0.41 ± 0.13, and 0.13 ± 0.06 L/g VS_{added} at 124, 62, and 35 d HRT, respectively (refer to Table 4). The highest biogas yield was achieved in both feeding mode at 124 d HRT, due to the rapid growth of methanogens in the new environment. At 41, 35, and 31 d HRT, a lower biogas yield was obtained because of the huge quantity of food waste used by the hydrolysis and acidification of microorganisms. Furthermore, the accumulation of excessive VFA led to the acute inhibition of biogas production, which finally resulted in the failure of the reactor [49]. However, the daily feeding mode resulted in the highest biogas yield (1.01 L/g VS_{added}), almost 11% higher than that of the feeding mode 3-times-per-week (0.91 L/g VS_{added}) (Figs. 1a and 2a). This data indicates that the anaerobic digestion performed more effectively during daily feeding compared to feeding done 3-times-per-week. A similar result was obtained by Mulat et al. [30], who found that a daily feeding regime produced 16% more biogas compared to other feeding regimes.

The biogas production rate usually reflects the productivity of the anaerobic reactor [48]. The biogas production rate in daily feeding mode and feeding mode 3-times-per-week at different HRTs is shown in Fig. 1a and Fig. 2a, respectively. It can be observed that the biogas production rate in the daily feeding mode increased gradually until day 83 after which it began to decrease slowly with some fluctuations. Meanwhile, the biogas production rate of the feeding mode 3-times-per-week increased until day 54 after which it started to decline gradually with some fluctuations. At 124 d HRT, the average biogas production rate in the daily and 3-times-per-week feeding mode was 0.39 ± 0.08 and 0.3 ± 0.12 L/L/d, respectively (Table 4). When the HRT was decreased from 124 to 62 d, the average biogas production rate in the daily feeding mode and feeding mode 3-times-per-week increased to 0.67 ± 0.13 and 0.61 ± 0.19 L/L/d, respectively (Table 4). A lower average biogas production rate in the daily feeding mode and feeding mode 3-times-per-week was observed at 31 and 35 d HRT, respectively. Significantly higher average biogas yields were observed for daily feeding compared to feeding 3-times-per-week. However, after day 128, scum was observed to accumulate in the daily feeding mode at 41 d HRT, creating difficulties such as blocking and reduced biogas production. Meanwhile, the accumulation of scum was observed in the feeding mode 3-times-per-week at an HRT of 62 d, after day 45. The reactor was cleaned after the scum started to accumulate. Scum accumulation continued in the reactor until the end of the experiment, with the layer of scum reaching almost 0.12–0.14 m thick in the upper portion of the reactor. Identical findings were obtained by Hu et al. [21] and Kobayashi and Li [50], who found that reducing HRT (or increasing OLR) could cause scum to accumulate in an anaerobic digester.

The biogas compositions during the entire operation were measured using a portable biogas analyzer. Figs. 1b and 2b show the biogas compositions in daily feeding mode and feeding mode 3-times-per-week, respectively, at different HRTs during the anaerobic digestion of food waste. The average CH_4 value in daily feeding mode was decreased from 67.54% ± 10.67% to 65.44% ± 3.12%, when HRT was reduced from 124 to 31 d (Table 4). Meanwhile, the average CO_2 value in daily feeding mode was increased from 28.18% ± 6.29% to 30.53% ± 3.34% during operations under decreased HRT. On the contrary, the average CH_4 values in feeding mode 3-times-per-week were 62.7% ± 5.73%, 51.39% ± 3.96%, and 50.79% ± 1.09% at an HRT of 124, 62, and 35 d, respectively (Table 4). Meanwhile, the average CO_2 values in feeding mode 3-times-per-week varied from 38% ± 4.38% to 45.99% ± 1.3% during operations under decreased HRT (Table 4). It was observed that the biogas composition showed a decreasing trend in the average CH_4 percentage while the average CO_2 percentage increased throughout the whole operation. Compared to feeding 3-times-per-week, daily feeding achieved higher average methane values and lower average carbon dioxide values.

Methane yield is a significant performance index of the stability of the anaerobic reactor when anaerobically

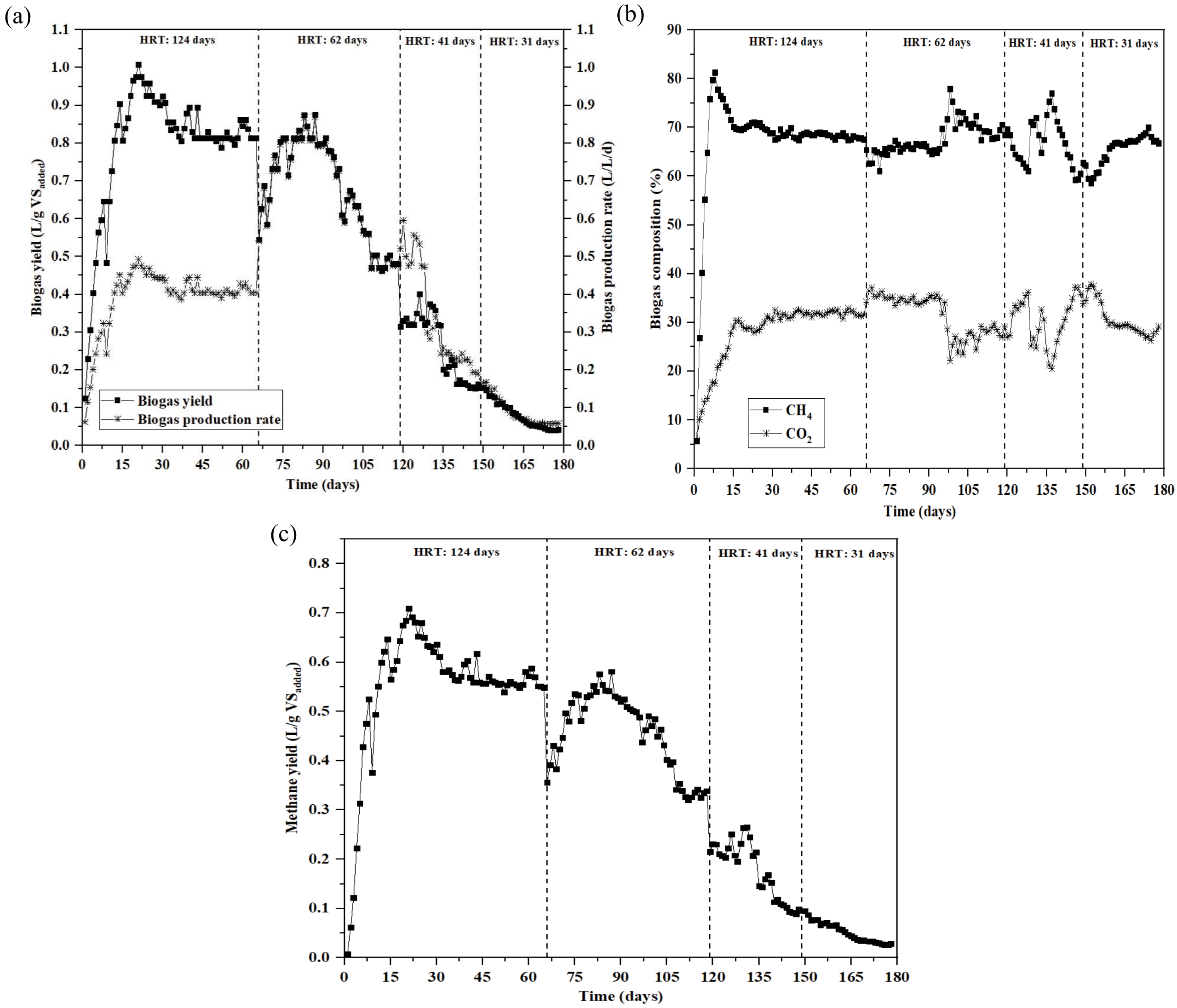

Fig. 1. (a) Biogas yield and biogas production rate, (b) biogas composition, and (c) methane yield in daily feeding mode during operation under declined HRTs.

digesting food waste. The methane yield in daily feeding mode and feeding mode 3-times-per-week at different HRTs is presented in Figs. 1c and 2c, respectively. The average methane yield in daily feeding mode declined concurrently with decreased HRT (refer Table 4), showing values of (0.55 ± 0.13, 0.45 ± 0.08, 0.17 ± 0.06, and 0.06 ± 0.02) L/g VS_{added} for (124, 62, 41, and 31 d) HRTs, respectively. In contrast, the average methane yield in feeding mode 3-times-per-week also decreased from (0.38 ± 0.17) to (0.07 ± 0.03) L/g VS_{added}, when HRT was reduced from 124 to 35 d (Table 4). Significantly higher methane yield (0.71 L/g VS_{added}) was observed in daily feeding, in which 15% more methane was produced compared to feeding 3-times-per-week (0.617 L/g VS_{added}) (Figs. 1c and 2c). This finding indicates a stable performance for daily feeding, and an unstable and low digestion performance for feeding 3-times-per-week. This result is possibly due to the irregularity of feeding during the feeding mode 3-times-per-week, possibly resulting in insufficient contact between substrate and microorganism, the reduction of effective volume because of settling and the formation of scum [51]. This result is consistent with that of a previous study, which observed a more stable performance in daily feeding over other feeding modes [30]. The study also observed 14% higher specific methane yield in daily feeding at 4 g VS/L/d OLR under mesophilic conditions. Meanwhile, Ziels et al. [31] found no difference in the methane yield for daily feeding vs. stepwise feeding. This is because the study used different substrates (i.e., co-digested cow manure and oleate) than the one in this study.

3.3. Effect of feeding mode on the performance of the reactor at different HRTs

3.3.1. Monitoring of pH, temperature, VFA, TA, and NH_3–N

pH is a very important parameter that defines the stability and efficiency of the anaerobic digestion process. The variations in pH and temperature of daily feeding mode

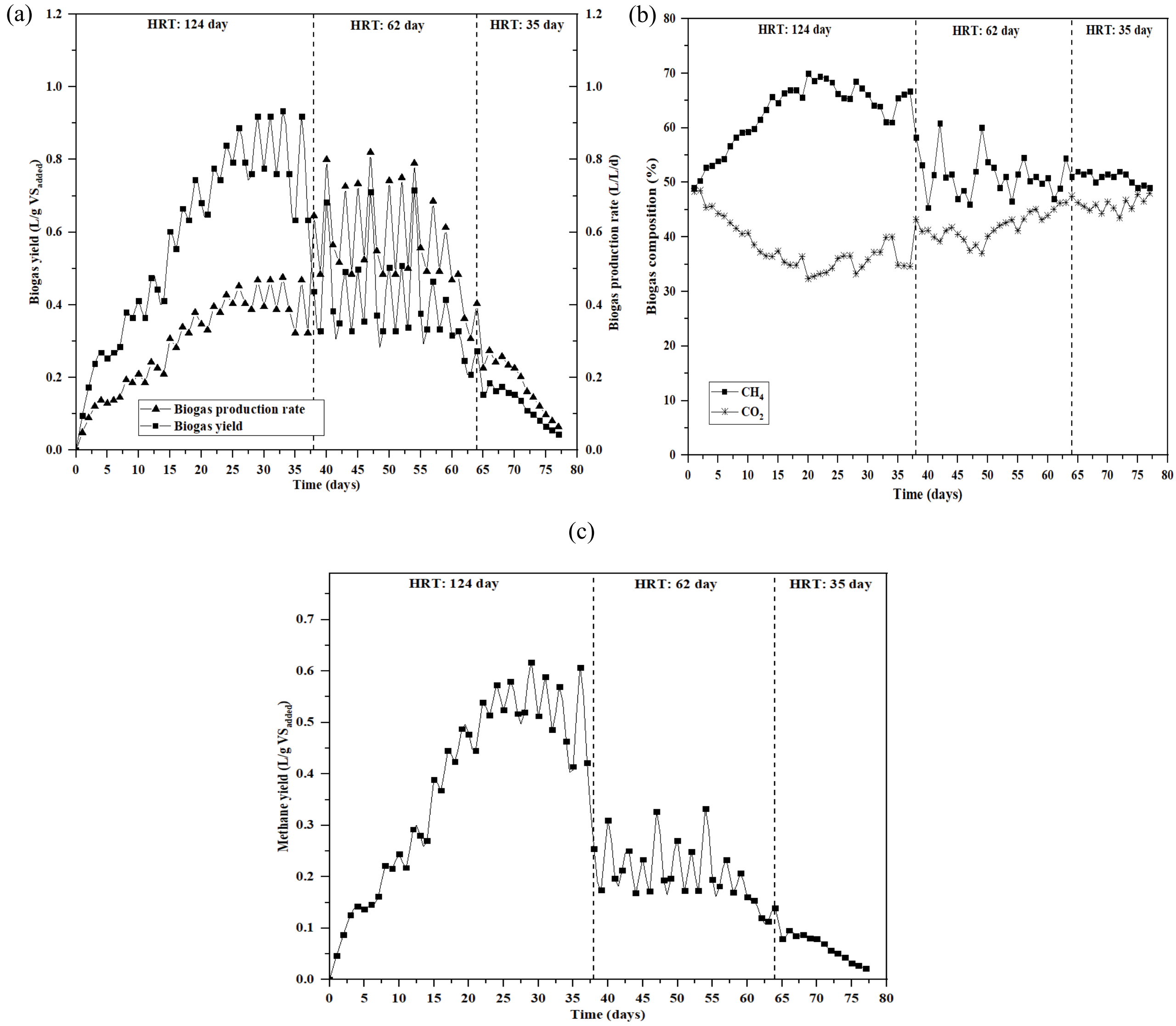

Fig. 2. (a) Biogas yield and biogas production rate, (b) biogas composition, and (c) methane yield in feeding mode 3-times-per-week during operation under declined HRTs.

and feeding mode 3-times-per-week at different HRTs are presented in Figs. 3a and 4a, respectively. Despite fluctuations in the weather during the operation, the reactor still operated in a mesophilic condition at temperatures ranging from almost 30°C to 34°C. pH significantly affects the performance of the reactor during the anaerobic digestion of food waste. The average pH value in daily feeding mode remained stable at an HRT of 124 d without the addition of any chemicals and was within the optimal pH range for methane production. The average pH value in daily feeding mode decreased gradually from pH 7.25 ± 0.05 to 7.07 ± 0.18, when the HRT reduced from 124 to 31 d (Table 4). During daily feeding mode, pH was maintained at an optimum range from day 94 to 178 with the addition of NaOH into the reactor after each feeding. On the other hand, the average pH value in the feeding mode 3-times-per-week declined concurrently with decreased HRTs (refer Table 4), showing pH 6.87 ± 0.14, 6.56 ± 0.35, and 5.33 ± 0.21 for (124, 62, and 35 d) HRT, respectively. Shi et al. [52] pointed out that the optimum pH range for high-solid content (4%–10% TS) anaerobic digestion was pH 6.6–7.8, while the acceptable pH range was pH 6.1–8.3. A significantly optimum average pH value was observed in the daily feeding mode compared to the feeding mode 3-times-per-week during operations under decreased HRTs.

Ammonia is produced from the protein content of food waste during hydrolysis. The concentration of the total NH_3–N is affected by pH and temperature during the anaerobic digestion of food waste [18]. The ammonia concentration in daily feeding mode and feeding mode 3-times-per-week is displayed in Figs. 3b and 4b, respectively, during operations under reduced HRTs. The ammonia concentration in daily feeding mode increased until day 113, after which it began to decrease slowly with some fluctuations until the end of the experiment. The average ammonia concentrations were (0.55 ± 0.24) g/L at 124 d

Table 4
Average characteristics of the effluent and average performances of the reactor during operation under decreased HRTs

	Daily feeding mode				3-times-per-week feeding mode		
HRT (d)	124	62	41	31	124	62	35
Water quality of the effluent							
pH	7.25 ± 0.05	7.18 ± 0.07	7.08 ± 0.16	7.07 ± 0.18	6.87 ± 0.14	6.56 ± 0.35	5.33 ± 0.21
VS (g/L)	7.39 ± 2.06	28.02 ± 9.57	22.3 ± 4.12	32.31 ±3.57	26.35 ± 3.67	22.34 ± 12.2	19.42 ± 3.06
COD (g/L)	8.97 ± 3.2	43.5 ± 16.34	38.63 ± 6.64	60.72 ± 4.33	43.31 ± 6.86	34.74 ± 18.67	32.11 ± 2.14
NH_3–N (g/L)	0.55 ± 0.24	1.18 ± 0.21	0.71 ± 0.25	0.7 ± 0.13	1.64 ± 0.86	3.27 ± 0.45	4.97 ± 0.54
VFA (g HOAc/L)	0.78 ± 0.52	4.28 ± 3.25	15.4 ± 3.13	25.76 ± 3.88	0.28 ± 0.05	2.56 ± 1.58	7.41 ± 1.08
TA (g $CaCO_3$/L)	5.15 ± 0.69	6.9 ± 2.89	16.55 ± 2.38	25.22 ± 3.15	2.19 ± 0.35	3.49 ± 0.75	7.34 ± 1.45
VFA/TA	0.15 ± 0.10	0.56 ± 0.23	0.93 ± 0.09	1.02 ± 0.05	0.13 ± 0.02	0.68 ± 0.31	1.02 ± 0.10
Reduction of the substrate							
VS reduction (%)	87.94 ± 3.5	54.8 ± 15.44	64.03 ± 6.64	47.71 ±5.91	57.88 ± 6.57	75.77 ± 13.12	78.88 ± 3.32
COD reduction (%)	91.7 ± 2.96	59.76 ± 15.11	64.26 ± 6.14	43.83 ± 4	60.4 ± 7.12	78.46 ± 11.48	80.02 ± 1.35
Biogas production							
Biogas production rate (L/L/d)	0.39 ± 0.08	0.67 ± 0.13	0.34 ± 0.14	0.09 ± 0.04	0.3 ± 0.12	0.58 ± 0.14	0.2 ± 0.09
Biogas yield (L/g VS_{added})	0.79 ± 0.17	0.68 ± 0.13	0.26 ± 0.09	0.08 ± 0.04	0.59 ± 0.24	0.41 ± 0.13	0.13 ± 0.06
Methane yield (L/g VS_{added})	0.55 ± 0.13	0.45 ± 0.08	0.17 ±0.06	0.06 ± 0.02	0.38 ± 0.17	0.21 ± 0.06	0.07 ± 0.03
Methane (%)	67.54 ± 10.67	67.53 ± 3.28	66.9 ± 4.87	65.44 ± 3.12	62.7 ± 5.73	51.39 ± 3.96	50.79 ± 1.09
Carbon dioxide (%)	28.18 ± 6.29	30.47 ± 4.22	30.5 ± 4.82	30.53 ± 3.34	38 ± 4.38	41.86 ± 2.5	45.99 ± 1.3

VS: volatile solid; COD: chemical oxygen demand; NH_3–N: ammonia–nitrogen; VFA: volatile fatty acid; TA: total alkalinity.

HRT, (1.18 ± 0.21) g/L at 62 d HRT, (0.71 ± 0.25) g/L at 41 d HRT, and (0.7 ± 0.13) g/L at 31 d HRT (Table 4). During daily feeding mode, the concentration of ammonia that accumulated inside the reactor did not surpass the toxic limitation threshold of 3 g/L. On the contrary, the average ammonia concentration in the feeding mode 3-times-per-week increased concurrently with decreased HRTs (refer Table 4), showing values of 1.64 ± 0.86, 3.27 ± 0.45, and 4.97 ± 0.54 g/L for 124, 62, and 35 d HRT, respectively. During the feeding mode 3-times-per-week, the concentration of ammonia that accumulated inside the reactor exceeded the toxic limitation threshold of 3 g/L. This result is probably due to the inconsistent feeding in the feeding mode 3-times-per-week, which could lead to an increase in ammonia concentration in the reactor. This result indicates that a more stable performance and a longer operating time were obtained for daily feeding compared to feeding 3-times-per-week.

Acidification because of the quick increase in VFA is one of the most common and significant causes that inhibit methanogens, therefore resulting in decreased biogas production and the failure of the entire process [49]. The variations in the VFA and TA concentration in daily feeding mode and feeding mode 3-times-per-week during operations under decreased HRTs are shown in Figs. 3c and 4c, respectively. At 124 d HRT, the average VFA and TA concentration in daily feeding mode was 0.78 ± 0.52 g HOAc/L and 5.15 ± 0.69 g $CaCO_3$/L, respectively (Table 4). A noticeable increase in VFA and TA was found as HRT entered the next step. When HRT was decreased from 124 to 62 d, the average VFA and TA concentration in daily feeding mode increased rapidly to 4.28 ± 3.25 g HOAc/L and 6.9 ± 2.89 g $CaCO_3$/L, respectively. When HRT further decreased to 41 d, an evident accumulation of VFA in daily feeding mode was noticed, nearly 3.5-fold to that of the 62 d HRT. On the other hand, feeding mode 3-times-per-week was stable at an HRT of 124 d due to the low average concentration of VFA (0.28 ± 0.05 g HAOc/L). The average TA concentration in feeding mode 3-times-per-week increased concurrently with decreased HRTs (Table 4), showing values of 2.19 ± 0.35, 3.49 ± 0.75, and 7.34 ± 1.45 g $CaCO_3$/L for 124, 62, and 31 d HRTs, respectively. When the HRT decreased from 62 to 35 d, a clear accumulation of VFA was observed in feeding mode 3-times-per-week and the average VFA concentration increased to 7.41 ± 1.08 g HAOc/L. Arij et al [48] reported that VFA is also defined as the readily biodegradable COD fraction, which is used as the food for the biomass in methanogenesis. Methanogenic microorganisms convert VFA to methane gas. The VFA concentrations in both feeding modes apparently increased with decreased HRT, as organic substances cannot be entirely degraded to biogas, correlating well with reduced biogas yield. The accumulation of VFA was observed in both feeding modes due to the elevated OLR/decreased HRT. This result is in accordance with the results of other previous studies, which also found that decreasing HRT/increasing OLR caused VFA to accumulate in the anaerobic reactor. Kumar et al. [24] observed the accumulation of VFA during operations under decreased HRTs when food waste was used as a substrate. Liu et al. [49] observed a noticeable accumulation of VFA in the reactor when the OLR was increased from 1 to 1.5 g of VS/L/d during the anaerobic digestion of food waste under mesophilic conditions.

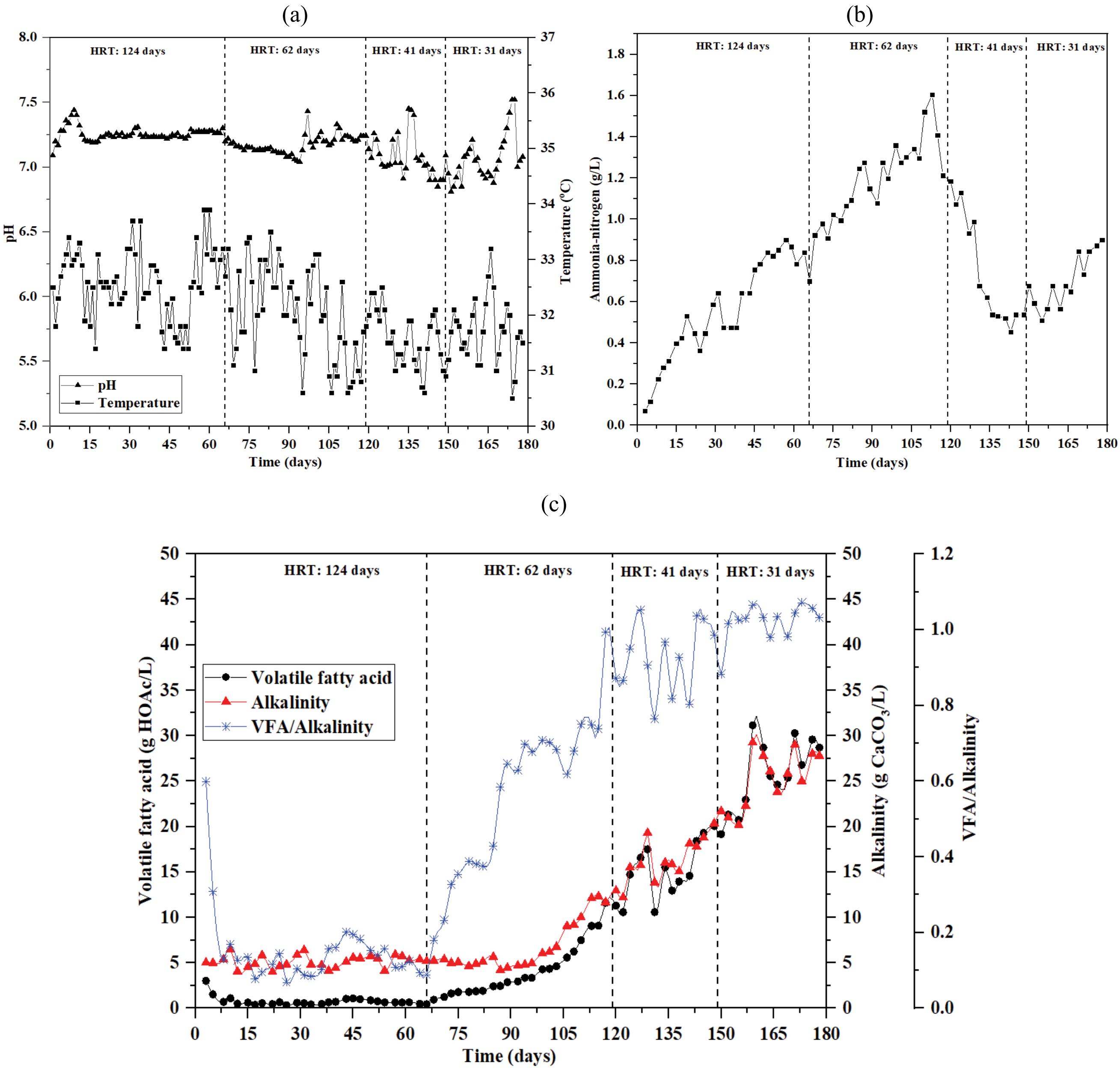

Fig. 3. (a) pH and temperature value, (b) ammonia–nitrogen concentration, and (c) volatile fatty acid and total alkalinity concentration in daily feeding mode during operation under declined HRTs.

Figs. 3c and 4c show the variations in the VFA/TA ratio in daily feeding mode and feeding mode 3-times-per-week, respectively. Gou et al. [20] stated that the reactor is considered stable when the VFA/TA ratio does not exceed the recommended threshold toxicity value (>0.4). At 124 d HRT, the average VFA/TA ratio in daily feeding mode (0.15 ± 0.10) and feeding mode 3-times-per-week (0.13 ± 0.02) were in the recommended threshold value (Table 4). When the HRT was decreased from 124 to 62 d, the VFA/TA ratio in daily feeding mode and feeding mode 3-times-per-week was increased to 0.56 ± 0.23 and 0.68 ± 0.31, respectively. The highest average VFA/TA ratio in daily feeding mode and feeding mode 3-times-per-week was 1.02 ± 0.05 at 41 d HRT and 1.02 ± 0.10 at 31 d HRT, respectively. For both feeding modes, the concentration of VFA that accumulated inside the reactor and the ratio of the VFA/TA far exceeded the recommended threshold value (<0.4). This result is consistent with the decreasing curves of the biogas yield and the methane yield during the period of operation under decreased HRTs. The unstable condition of the reactor suggests that huge quantities of VFAs had not yet been transformed efficiently [20]. This finding led to poor system stability and less efficient performance of the reactor during operations under decreased HRTs. A similar result was reported by Gou et al. [20] who investigated the performance of anaerobic co-digestion of waste-activated sludge and food waste under mesophilic conditions. They found that when HRT continued to decrease, irreversible acidification occurred, resulting in the collapse of the entire system. At the end of the study, a VFA/TA ratio of almost 2.2 was observed.

3.3.2. Removal of organic pollutants

The organic substances of food waste were degraded and transformed into biogas during the anaerobic digestion process, which resulted in the fluctuations of VS and COD concentration. Figs. 5a and 6a display the variations in VS and COD concentration in daily feeding mode and feeding mode 3-times-per-week, respectively. The effluent average VS and COD concentration in daily feeding mode was increased from 8.97 ± 3.2 to 32.31 ± 3.57 and 8.97 ± 3.2 to 60.72 ± 4.33 g/L, respectively, when HRT was reduced from 124 to 31 d (Table 4). On the contrary, when the HRT declined from 124 to 35 d, the effluent average VS and COD concentration in feeding mode 3-times-per-week was decreased from 26.35 ± 3.67 to 19.42 ± 3.06 and 43.31 ± 6.86 to 32.11 ± 2.14 g/L, respectively (Table 4). It can be observed that the effluent VS and COD concentration during feeding mode 3-times-per-week increased first and decreased thereafter during operations under reduced HRTs (Fig. 6a). This might be due to the urging of the floating scum that brought the sludge to the upper portion of the reactor [21]. In contrast, the effluent VS and COD concentration in daily feeding mode exhibited a decreasing trend at first and then increased when HRT decreased (Fig. 5a). However, high VS concentration of the digestate resulted in an acidic environment in the digester,

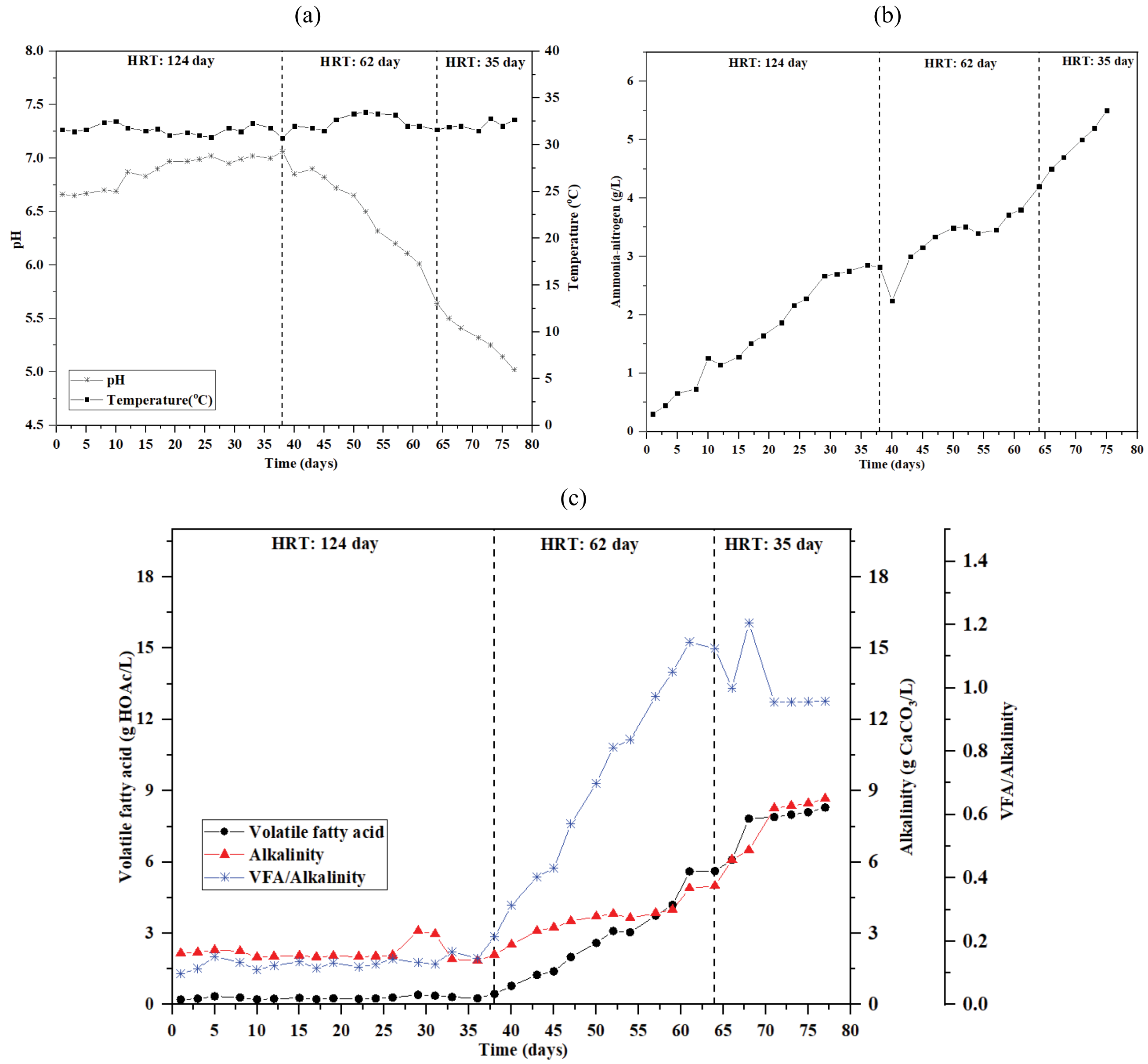

Fig. 4. (a) pH and temperature value, (b) ammonia–nitrogen concentration, and (c) volatile fatty acid and total alkalinity concentration; in feeding mode 3-times-per-week during operation under declined HRTs.

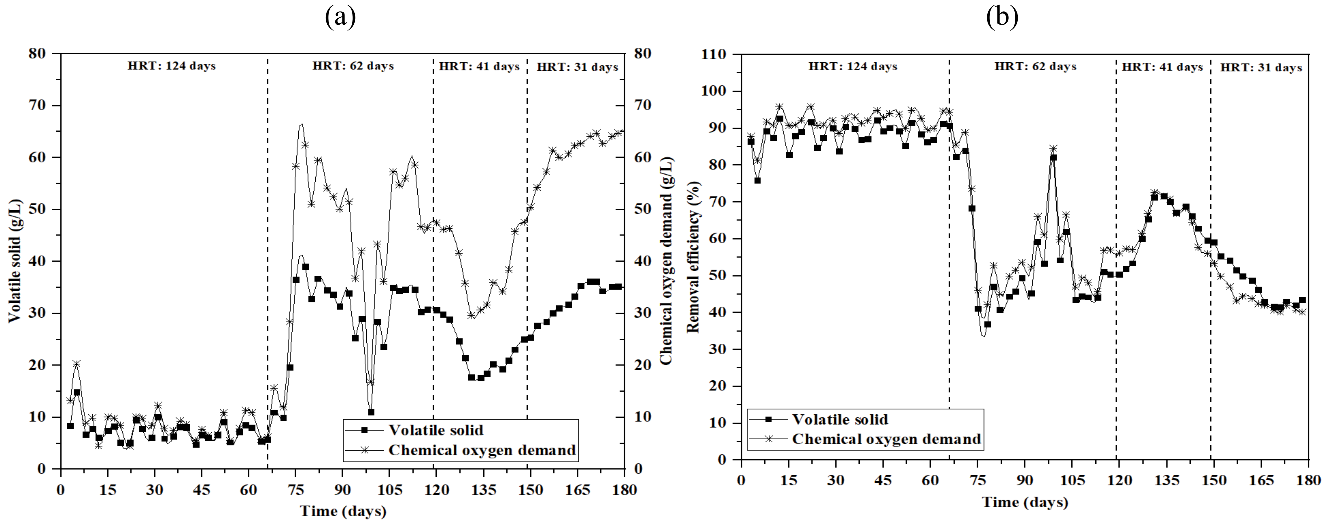

Fig. 5. (a) Variations and (b) removal efficiencies in terms of volatile solid and chemical oxygen demand in daily feeding mode's discharged effluent during operation under declined HRTs.

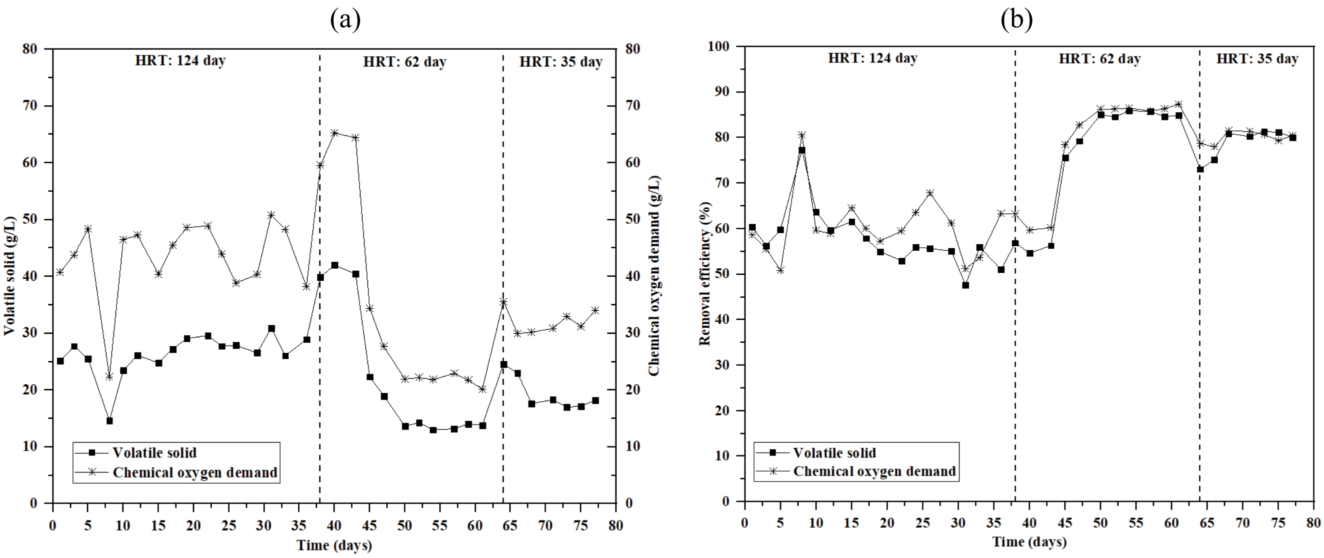

Fig. 6. (a) Variations and (b) removal efficiencies in terms of volatile solid and chemical oxygen demand in 3-times-per-week feeding mode's discharged effluent during operation under declined HRTs.

eventually leading to poor biogas production [53]. The accumulated hydrolysis and acidogenesis products inhibited the production of biogas [49].

The removal efficiency of VS and COD from the discharged effluent in daily feeding mode and feeding mode 3-times-per-week is shown in Figs. 5b and 6b, respectively. An average VS and COD removal efficiency of 87.94% ± 3.5% and 91.7% ± 2.96%, respectively, were achieved in daily feeding mode at 124 d HRT (Table 4). When the HRT was decreased from 124 to 31 d, the average VS and COD removal efficiency in daily feeding mode decreased to 47.71% ± 5.91% and 43.04% ± 4.01%, respectively. This result can be attributed to the increase in the organic load of the digester at shorter HRTs during daily feeding mode. It could also be due to the overall increase in the reactor's lipid content, which has comparatively low degradability. Increased total solid content with decreased HRTs might also be the reason for the decline in the digester's VS removal efficiency [53]. This result is in good agreement with the decreasing curves of biogas production and methane yield during the period of operation under decreased HRTs. In contrast, the average VS and COD removal efficiency in feeding mode 3-times-per-week was 57.88% ± 6.57% and 60.4% ± 7.12%, respectively, at 124 d HRT (Table 4). The average VS and COD removal efficiency in feeding mode 3-times-per-week was increased from 75.77% ± 13.12% to 78.88% ± 3.32% and from 78.46% ± 11.48% to 80.02% ± 1.35%, respectively, when HRT was decreased from 62 to 35 d (Table 4). This result shows that the biogas yield in feeding mode 3-times-per-week had a negative correlation with VS and COD removal efficiency when the HRT was decreased. However, daily feeding produced the highest average VS and COD removal efficiency, which were almost 11.5% and 14.6% higher, respectively, than that of feeding 3-times-per-week (Figs. 5b and 6b). The higher VS and COD removal efficiency indicates the better degradation of organic matter in the daily feeding mode. Opposite findings were reported by Mulat et al. [30] and Vrieze et al. [54], who observed lower system removal efficiency of VS and COD in a daily-fed reactor compared to a stepwise-fed reactor. Their result might be due to the use of different substrates and OLRs.

3.3. Kinetic analysis and model selection

Suitable kinetic model selection is required not only for design, process intensification, and long-term anaerobic digestion operation, but also to precisely clarify the mechanisms and metabolic pathways associated with the anaerobic digestion process under various operating conditions [39]. Four kinetic models including the first-order kinetic model, the modified Gompertz model, the logistic function model, and the Cone model were proposed to evaluate the performance of a reactor operated under two different feeding modes: daily feeding and feeding 3-times-per-week. The estimated values of the hydrolysis constant (k) for the first-order-kinetic model and the Cone model are presented in Table 5. The first-order-kinetic model and the Cone model were able to calculate the rate of hydrolysis, considered to be the rate-limiting stage in the anaerobic digestion of food waste. A higher k-value indicating the quick degradation rate of food waste [37]. The k-value of daily feeding mode calculated using the first-order model and the Cone model were 0.014 and 0.018 d^{-1}, respectively. On the other hand, the k-value of feeding mode 3-times-per-week

Table 5
Estimated kinetic parameters for the four kinetic models

Kinetic model	Parameter		Unit	Daily feeding mode	3-times-per-week feeding mode
First-order-kinetic model	Hydrolysis rate constant (k)		1/d	0.014	0.028
	R-square			0.933	0.887
	RMSE			5.597	2.398
	Methane yield	Predicted	L/g VS_{added}	61.13	18.4
		Measured	L/g VS_{added}	66.645	20.439
		Difference	%	8.275	9.97
Modified Gompertz model	Lag phase time (λ)		days	10.845	10.226
	T_{90}		days	119	56
	T_{ef}		days	108	46
	Maximum methane production rate (R_m)		L/g VS_{added} d	0.691	0.535
	R-square			0.994	0.998
	RMSE			1.646	0.280
	Methane yield	Predicted	L/g VS_{added}	65.04	19.96
		Measured	L/g VS_{added}	66.645	20.439
		Difference	%	2.408	2.343
Logistic function model	Lag phase time (λ)		days	12.017	10.914
	T_{90}		days	119	56
	T_{ef}		days	107	45
	Maximum methane production rate (R_m)		L/g VS_{added} d	0.656	0.516
	R-square			0.993	0.994
	RMSE			1.784	0.571
	Methane yield	Predicted	L/g VS_{added}	65.94	20.25
		Measured	L/g VS_{added}	66.645	20.439
		Difference	%	1.058	0.925
Cone model	Hydrolysis rate constant (k)		1/d	0.018	0.035
	Shape factor (n)			2.514	3.128
	R-square			0.993	0.994
	RMSE			3.254	0.540
	Methane yield	Predicted	L/g VS_{added}	63.26	19.56
		Measured	L/g VS_{added}	66.645	20.439
		Difference	%	5.079	4.300

R^2: coefficient of determination; RMSE: root mean square error; T_{90}: time taken for 90% methane production; effective methane production duration (T_{ef}) = (T_{90} – λ).

estimated using the first-order model and the Cone model was 0.028 and 0.035 d^{-1}, respectively. This finding is consistent with the results reported by Nguyen et al. [39], wherein the value of *k* obtained from the Cone model was higher than that obtained using the first-order model. The *k*-values estimated in this study from the first-order-kinetic model and the Cone model were significantly lower than that of previous studies. For example, Li et al. [40] reported that the *k*-values of food waste digesters were in the range of 0.79–2.98 d^{-1} for the first-order-kinetic model and 0–4.61 d^{-1} for the Cone model. On the other hand, Li et al. [36] found the *k*-value using the first-order model to be in the range of 0.13–4.73 d^{-1}. This indicated the lower hydrolysis rate of the food waste used in this study than the previous studies.

The maximum predicted methane potential (P_b) of daily feeding mode and feeding mode 3-times-per-week calculated from the provided models, which varied according to the parameter of the model and substrate composition. The maximum methane production rates R_m and P_b of daily feeding mode and feeding mode 3-times-per-week are displayed in Table 5. The P_b of daily feeding mode predicted by the first-order model, the modified Gompertz model, the logistic function model and the Cone model were 61.13, 65.04, 65.94, and 63.26 L/g VS_{added}, respectively. On the other hand, the P_b values of feeding mode 3-times-per-week were ranged from 18.07–20.25 L/g VS_{added} for all tested models. The R_m value of daily feeding mode ranged from 0.691–0.656 L/g VS_{added} d, while the R_m value of feeding mode 3-times-per-week ranged from 0.516–0.535 L/g VS_{added} d. Significantly higher R_m and P_b were observed in daily feeding compared to feeding 3-times-per-week. The R_m values found in this study were significantly higher compared to that of previous studies. For example, Kafle and Chen [45] compared the batch anaerobic digestion of five different livestock manures with the R_m values ranged from 55–25.2 mL/g VS_{added} d. Donoso-Bravo et al. [44] reported R_m values of 29.92–42.09 mL/g VS_{added} d when pre-treated sewage sludge was used as a substrate. Li et al. [55] found R_m values for chicken manure ranging from 19.4–48.9 and 16.0–32.1 mL/g VS_{added} d for corn stover. It can be observed that the R_m values of the food waste in this study are higher than those reported for different livestock manures, sewage sludge, and corn stover. This might be because food waste is more easily degradable compared to other substrates, including livestock manure, sewage sludge, and corn stover [36].

Besides the P_b, R_m, and *k* parameters, digestion time, and lag phase were also significant indicators of substrate utilization rate and biodegradability. The delayed response and the subsequent adaptation of microbes to the varying environment are expressed by the lag phase (λ) [36,56]. The values of λ and effective methane production period (T_{ef}) for daily feeding mode and feeding mode 3-times-per-week are presented in Table 5. The λ value for daily feeding mode and feeding mode 3-times-per-week ranged from 10.845–12.017 and 10.226–10.914 d, respectively. The T_{ef} was calculated by subtracting the λ value from the time required to achieve 90% of total cumulative methane production (T_{90}). Studies have described that a longer λ with a longer T_{ef} might display longer periods of anaerobic digestion and reversible process inhibition, while a longer λ with shorter T_{ef} might correlate to a shorter anaerobic digestion period and irreversible process inhibition [36,56]. For the logistic function model and the modified Gompertz model, the T_{ef} value of daily feeding mode was found to be 107 and 108 d, respectively, while the T_{ef} value of feeding mode 3-times-per-week was estimated to be 45 and 46 d, respectively. Significantly longer T_{ef} and λ values were achieved in the daily feeding mode compared to the feeding mode 3-times-per-week. This result indicates that daily feeding yielded higher methane production, a longer anaerobic digestion period, and a higher conversion efficiency of food waste to methane compared to feeding 3-times-per-week. Therefore, the validity of these findings is confirmed (refer to Table 5).

The methane production potential of the reactor under study was determined by fitting the experimental data based on cumulative methane production. The predicted cumulative methane yield was derived from the first-order-kinetic model, the modified Gompertz model, the logistic function model and the Cone model. The predicted cumulative methane yield of daily feeding mode and feeding mode 3-times-per-week is displayed in Figs. 7 and 8, respectively. The polynomial regression models describe the correlation between the cumulative methane yield as a function of anaerobic digestion time and food waste. The correlation was defined by three primary phases, namely lag phase, exponential phase, and stationary and death phase. It was observed that methane was produced during the lag phase. The duration of the lag phase was varied from 10–12 d for daily feeding mode and from 10–11 d for feeding mode 3-times-per-week. The cumulative methane yield of daily feeding mode and feeding mode 3-times-per-week increased sharply from 12–153 and 11–60 d, respectively. This result is due to the fast growth of the anaerobic microbial communities [39]. The cumulative methane yield of daily feeding mode and feeding mode 3-times-per-week tended to gradually increase until the cumulative methane yield of the daily feeding mode (after 156 d) and feeding mode 3-times-per-week (after 60 d) curve nearly reached a plateau. The cumulative methane yields almost ceased in the plateau condition probably due to the depletion of the substrate and the death of cells [39]. The difference between the measured and predicted cumulative methane yield in this study was found to range within 8.275%–9.97% for the first-order model, 2.343%–2.408% for the modified Gompertz model, 0.925%–1.058% for the logistic function model, and 4.3%–5.079% for the Cone model (Table 5). The low deviations found between the predicted and measured values (≤10%) indicate that the proposed kinetic models had precisely predicted the performance of the reactor [3].

An appropriate kinetic model can evaluate and predict the biomethane production precisely for practical applications and provide the parameters required for optimal operation and design of the anaerobic digestion process. On the contrary, an incorrect selection or inadequate assessment of the suitability of the kinetic model might have several outcomes such as inaccurate operation and design, causing the collapse of project or the inability to fulfil project needs [36,39,56]. The criteria parameters of RMSE, RSS, AIC, and BIC were calculated (Tables 6 and 7) and used as the main discriminators to determine a better fit of the model to the

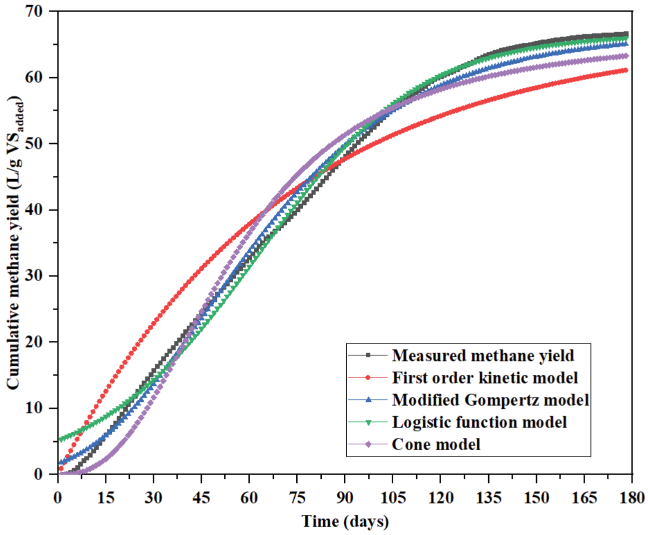

Fig. 7. Experimental data and model simulation/prediction of cumulative methane yield of daily feeding mode.

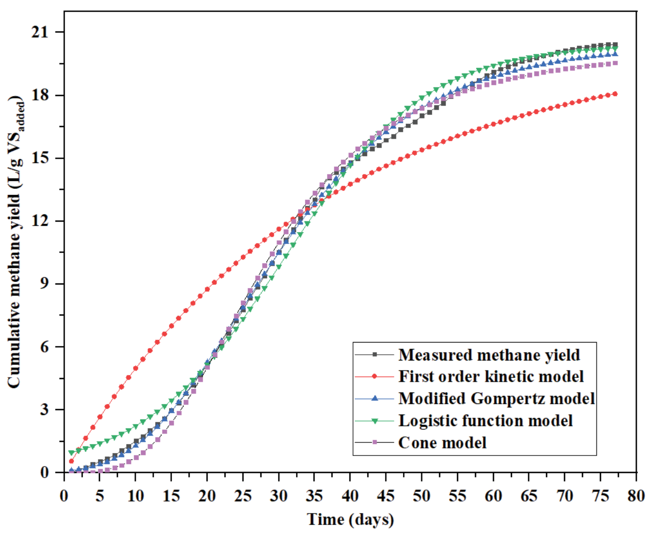

Fig. 8. Experimental data and model simulation/prediction of cumulative methane yield of 3-times-per-week feeding mode.

Table 6
Criteria for analysis of the best fit of the four kinetic models for daily feeding mode

Kinetic model	RSS	N	Parameter	AIC test			BIC test	
				AIC	Δ(AIC)	Akaike weight	BIC	Δ(BIC)
First-order-kinetic model	5,571.58	178	2	616.97	433.52	7.28×10^{-95}	623.33	430.34
Modified Gompertz model	482.37	178	3	183.45	0	0.99	192.99	0
Logistic function model	566.37	178	3	212.03	28.58	6.22×10^{-7}	221.57	28.58
Cone model	1,831.847	178	3	420.97	237.52	2.65×10^{-52}	430.52	237.53

RSS: residual sum of the square; N: number of data points; AIC: Akaike information criterion; BIC: Bayesian information criterion; Δ: difference.

Table 7
Criteria for analysis of the best fit of the four kinetic models for feeding mode 3-times-per-week

Kinetic model	RSS	N	Parameter	AIC test			BIC test	
				AIC	Δ(AIC)	Akaike weight	BIC	Δ(BIC)
First-order-kinetic model	441.94	77	2	138.71	328.34	5.03×10^{-72}	143.24	326.17
Modified Gompertz model	6.043	77	3	–189.63	0	0.99	–182.93	0
Logistic function model	25.04	77	3	–80.17	109.46	1.70×10^{-24}	–73.47	109.46
Cone model	22.008			–90.11	99.52	2.45×10^{-22}	–83.40	99.53

RSS: residual sum of the square; N: number of data points; AIC: Akaike information criterion; BIC: Bayesian information criterion; Δ: difference.

experimental data. The lower values of RMSE, RSS, AIC, and BIC indicate a more appropriate model. Both for the daily feeding mode and feeding mode 3-times-per-week, the modified Gompertz model had the lowest values of RMSE, RSS, AIC, and BIC in comparison to the first-order model, the Cone model and the logistic function model (Tables 5–7). Furthermore, the modified Gompertz model of daily feeding mode and feeding mode 3-times-per-week had the highest R^2-value of 0.994 and 0.998, respectively than the first-order model, the Cone model, and the logistic function model (Table 5). This result indicates that the modified Gompertz model presented a more robust estimation, explaining >99% of the variations in the results in comparison to the first-order-kinetic model, the logistic function model and the Cone model. Nguyen et al. [39] reported that higher values of R^2 and lower values of RSS, RMSE, AIC, and BIC indicate a more suitable model. Similar results were reported by Deepanraj et al. [35] and Bala et al. [38], who found that the modified Gompertz model was the best fit for their study compared to the logistic function model and the first-order-kinetic model.

4. Conclusion

This study investigated the impact of feeding mode on the process performance of a semi-pilot single-stage reactor operating under different HRT. The results indicate that the stability and the performance of the anaerobic digestion process, namely biogas production rate, methane yield, intermediate metabolism, and removal efficiency were significantly affected by feeding mode. By comparing feeding modes 3-times-per-week and daily feeding, it was found that the latter exhibited more stable and efficient performance than the former. Significantly higher biogas yield, methane yield, and organic removal efficiency were observed in the daily feeding mode compared to feeding 3-times-per-week. VFA accumulation was observed in both feeding modes although ammonia only started to accumulate when the reactor was fed 3-times-per-week. This case, in turn, resulted in reduced overall biogas and methane yield. For both feeding modes, the modified Gompertz model was found to be the most suitable model (R^2 = 0.994–0.998) for fitting the measured methane yield. The model can also be used to describe the kinetics of the anaerobic digestion process more reasonably. The calculated parameters showed that the anaerobic digestion of food waste in the two feeding modes had a low hydrolysis rate and a long lag phase. However, further research with different feeding intervals is required in large-scale reactors that use food waste as well as reactors that use other substrates.

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