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Theoretical biochemical methane potential generated by the anaerobic digestion of mustard green residues in different dilution volumes

Abstract:

The green mustard residues can be converted into biogas through anaerobic digestion. In this study, different dilution volumes (1 L, 1.5 L, 2 L) were observed to determine the effect of dilution volumes on biogas yield. Three kinetic models (first-order, Fitzhugh, modified Gompertz model) were used to simulate the methane potential, kinetic constants and lag phase time. The experiment was carried out in 5 L digesters at room temperature. The results showed that modified Gompertz is the best model for simulating the AD process. Dilution volume affected biogas production ($p < 0.05$) with the highest biogas yield of 4372.58 mL/gVS (dilution volume of 2 L). The statistical analysis showed a significant correlation between the COD total, different dilution volumes and theoretical methane potential ($p < 0.05$).

Keywords: biogas; chemical oxygen demand; kinetic model; mustard green; regression model

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Introduction

Anaerobic digestion (AD) is a biochemical reaction consisting of the hydrolysis stage, acetogenesis stage, and methanogenesis stage [1]). The AD process generates two main products: biogas and digestates [2]. The compositions of biogas are 50-70% of methane (CH_4), 30-45% of carbon dioxide (CO_2), and other impurities of hydrogen sulfide, ammonia, and water vapour [3].

The raw material of biogas can be obtained from organic materials such as the residue and by-products of vegetables since it has high organic content and moisture [4]. Mustard greens (*Brassica juncea*) are plentiful plants in Indonesia. Nevertheless, after harvesting, the farmers are inclined to waste the mustard greens due to the imbalanced market price and cultivation cost [5].

The potential biogas production assay, also called biochemical methane potential (BMP), is the primary parameter for describing the wastes and determining the optimal variables of the anaerobic digestion process [6]. The BMP also determines the fraction of organic carbon in a given substrate that can be converted to methane [7].

The mathematical models can represent the potential of digester performance and provide the theoretical biogas yield [8]. Numerous methods for calculating theoretical methane potential are based on chemical oxygen demand (COD), primary composition, and kinetic models [9]. Most studies have focused on determining biogas potential using chemical composition and substrate COD [10–12]. However, no study has investigated the relationship between dilution volumes and biochemical methane potential by determining a regression model. Therefore, this study aimed to evaluate the effect of dilution volume on biochemical methane potential and determine the kinetic parameters by simulating different kinetic models.

Material and Methods

Feedstock and inoculum preparation

Mustard green was collected from vegetable sellers in Yogyakarta, Indonesia. The green mustard residuals were shredded and stored at 20°C. Yeast was used as inoculum containing 44% carbohydrates, 44% protein and 12% fat.

Anaerobic digestion experimental set-up

The substrate and 50 g yeast were fed in batch digesters. The experiment was performed in different water dilution volumes of 1 L, 1.5 L, and 2 L. The substrate-to-inoculum ratio (S/I ratio) was maintained at 5 (based on the dry matter content). The anaerobic digestion test was conducted for 40 days.

Analytical method

Volatile solids (VS) and chemical oxygen demand (COD) were analyzed according to standard methods. Biogas volume was measured using the water displacement method. Corrected biogas volumes were calculated using the equation below (Khadka et al., 2022):

$$V_{STP} = \frac{V_T \times 273 \times (760 - P_w)}{760 \times (273 + T)} \qquad (1)$$

Where V_{STP} is biogas volume of standard temperature and pressure (L); V_T is a volume of biogas measured at temperature T (L); T is the temperature of biogas or ambient space (°C); P_w is saturated vapour pressure at the ambient temperature (mmHg)

MS Excel performed the analysis of variance (ANOVA). The significant results were checked with a p-value less than 0.05. The kinetic parameters were determined using regression analysis by Solver in MS Excel.

The theoretical methane yield was performed according to the following equation (Tassew et al., 2019)

$$CH_4\ yield = COD_{total} \times V_{sample} \times (0.36\ LCH_4/g\ COD) \qquad (2)$$

Kinetic models

The first-order, Fitzhugh, modified Gompertz models fit the measured biogas yields. Model equations are presented in Table 1.

Table 1. The kinetic model to express biogas production from batch anaerobic digestion of mustard green wastes

Model	Equation	References
First-order	$M_t = M_0 \times \left(1 - exp^{(-kt)}\right)$	(Habchi et al., 2022)
Fitzhugh	$M_t = M_0 \times \left(1 - exp^{(-kt)^n}\right)$	(Yazidi & Thanikal, 2016)
Modified Gompertz	$M_t = M_0 \times exp\{-exp[(R_m.e/M_0) \times (\lambda - t) + 1]\}$	(Ejimofor et al., 2020)

M_t represents the cumulative methane production (CMP), mL/gVS; t represents for anaerobic digestion time, day; M_0 represents the simulated methane potential (mL/gVS); R_m is the maximum methane production rate, mL/gVS/day; e equals to 2.7183; n is a dimensionless shape factor, and λ represents the lag phase time, day.

Results and Discussion

Effect of dilution volumes on biogas production

The influence of dilution volumes on biogas production is presented as daily and cumulative biogas yields in Figure 1 and Figure 2, respectively. Biogas production was initiated on day 4 with biogas yields of 261.44 mL/gVS, 411.76 mL/gVS, and 392.16 mL/gVS at dilution volumes of 1 L, 1.5 L, and 2 L, respectively. Biogas production then increased gradually until reaching peak yields of 372.55 mL/gVS, 931.37 mL/gVS, and 1490.20 mL/gVS on day 12 at dilution volumes 1 L, 1.5 L, and 2 L. Biogas production then dropped progressively with the lowest yield obtained on day 40.

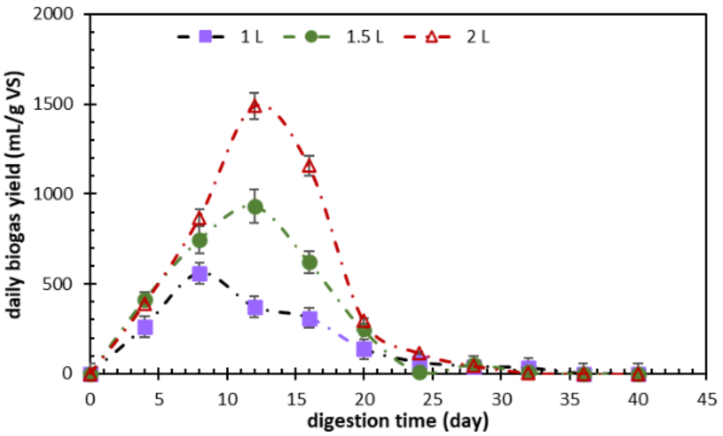


Figure 1. Daily biogas yields during anaerobic digestion of mustard green wastes.

Figure 2 illustrates an enormous cumulative yield of 4372.58 mL/gVS was obtained at a dilution volume of 2 L, followed by cumulative yields of 1781.70 mL/gVS and 3026.85 mL/gVS for dilution volumes of 1 L and 1.5 L, respectively. An increase in dilution volumes gained a positive effect on biogas production. Statistical analysis performed that dilution volumes affected biogas production significantly with a p-value of 0.0076 ($p < 0.05$).

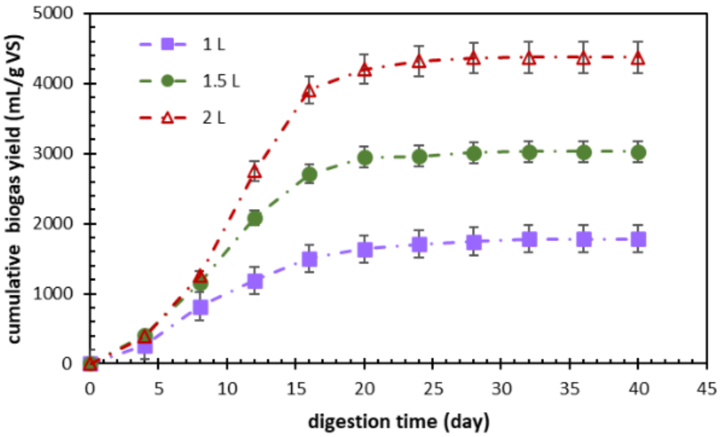


Figure 2. Cumulative biogas yields during anaerobic digestion of mustard green wastes.

The prior study conducted by Jeppu et al. (Jeppu et al., 2022) reported that as dilution increased, the biogas production also increased during the anaerobic digestion of cow dung. A similar result exposed that the highest dilution generated high methane (Evidente & Almendrala, 2022).

Kinetic Results

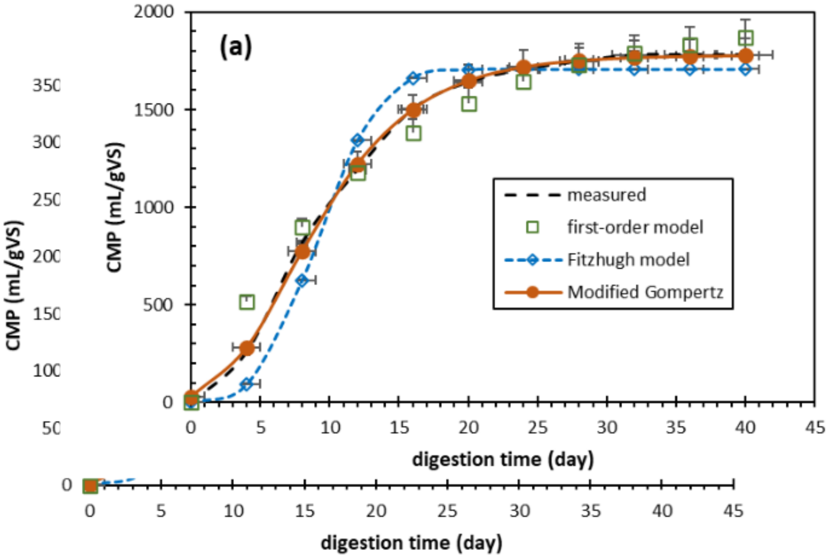
Table 2 presents the relevant results of model parameters. Among the three kinetic models used in this experiment, the modified Gompertz model performs the slightest difference (0.29-0.9%) between the calculated and measured biogas yield (M_o) followed by the Fitzhugh model (0.69-4.17%), whereas a tremendous difference (4.62-7.28%) between the calculated and measured biogas yield is obtained in the first-order kinetic model. For the Fitzhugh and first-order model, the values of k were almost constant for all substrates in each dilution volume. However, the Fitzhugh model provided a higher k than the first-order model. The R^2 obtained by the Fitzhugh model was also higher than the first-order kinetic model. Therefore, the Fitzhugh model is more appropriate for calculating the rate constants (k). The higher k indicated the rapid degradation rate and fast biogas production [20]. The lower dilution volume (1 L) obtained a higher k which denoted the enhanced substrate degradation and biogas yield.

Table 2. Kinetic parameters of first-order, Fitzhugh, and modified Gompertz models

Model	**Parameters**	**Dilution volumes** **1 L**	**1.5 L**	**2 L**
First-order	Mo (mL/gVS)	1960.54	3383.57	5102.59
	k (1/day)	0.076	0.076	0.065
	R^2	0.9185	0.9196	0.9397
	difference	4.62%	6.00%	7.28%
Fitzugh	Mo (mL/gVS)	1707.43	2977.15	4342.38
	k (1/day)	0.096	0.092	0.084
	n	3.00	3.00	3.00
	R^2	0.9976	0.9974	0.9976
	difference	4.17%	1.64%	0.69%
modified Gompertz	Mo (mL/gVS)	1779.00	3055.07	4414.37
	Rm (mL/gVS/day)	130.19	255.06	402.86
	l (day)	2.04	3.17	4.68
	R^2	0.9995	0.9992	0.9992
	difference	0.29%	0.86%	0.90%

The ultimate methane yield (M_0) could be calculated from the Fitzhugh, modified Gompertz and first-order kinetic model. For all models, the value of the ultimate biogas yield of substrates increased with dilution volume increased. For the modified Gompertz model, the maximum methane production rate (R_m) increased with increasing dilution volumes; however, the lag phase (λ) was more extended as dilution volumes increased. This phenomenon might imply that the Gompertz model is inaccurate enough to predict the lag phase under the studied circumstances. The prolonged lag phase might occur due to the long hydrolysis time and slow methanogenesis [21]. The previous study also reported that the lag phase increased as the biogas production rate increased in the anaerobic co-digestion of Thai rice noddle wastewater and chicken manure [11].

Figure 3 shows the regression fitting of the experimental data following first-order, Fitzhugh and modified Gompertz models. According to the results, all three models could simulate the anaerobic digestion of mustard green wastes well due to the $R^2 > 0.9$ for all models. However, the experimental data fit very well with the modified Gompertz. Furthermore, the values of R^2 show that the modified Gompertz model prediction to the experimental value is statistically higher than the first-order and Fitzhugh models (see Table 2). The dilution volume of 2L had the highest M_0 (4414.37 mL/gVS) and R_m (402.86 mL/gVS/day), respectively.



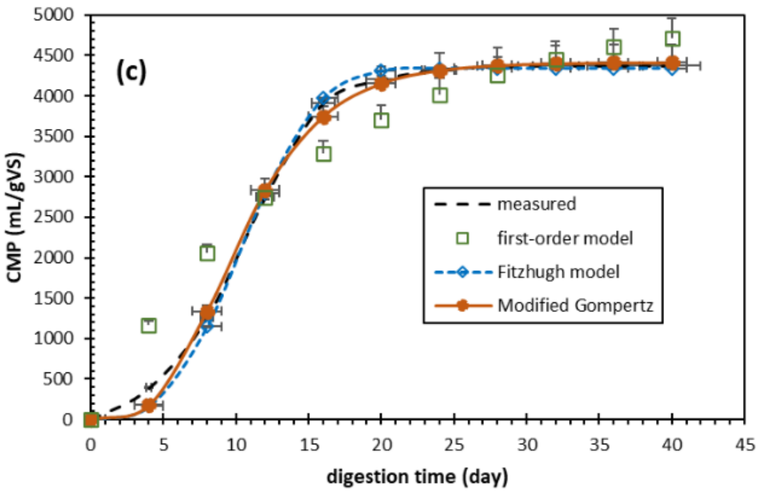


Figure 3. Regression fitting of cumulative biogas yield following first-order, Fitzhugh, and modified Gompertz models in different dilution volumes: (a) 1 L; (b) 1.5 L; (c) 2 L

According to previous literature, the modified Gompertz model had higher R^2 (0.985-0.999) than first-order (R^2 0.813-0.992) and Fitzhugh (R^2 0.813-0.992) models during the anaerobic digestion of vegetable wastes [22]. Ajayi-banji [23] reported that modified Gompertz was the best-fit model to depict the kinetic of solid-state anaerobic co-digestion of corn stover with dairy manure among two other models of Fitzhugh and first-order.

Correlation between COD total, dilution volume and theoretical methane yield

COD represents the quantity of organic material in a substrate [24]. The efficiency of the process can be evaluated by the COD content in the digester [25]. The correlation between theoretical methane yield and COD total is illustrated in Figure 4.

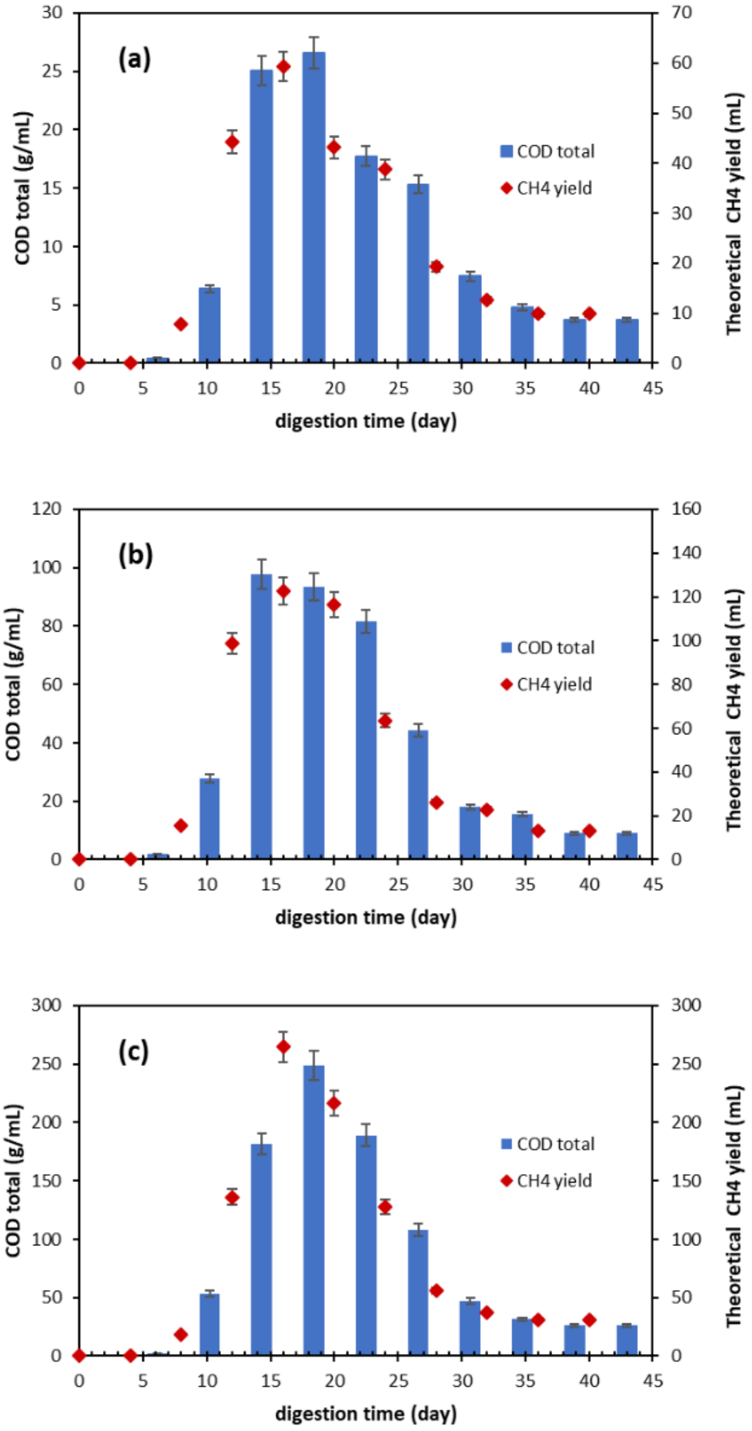

(a)
(b)
(c)
COD total (g/mL)
Theoretical CH4 yield (mL)
digestion time (day)
COD total
CH4 yield
0
5
10
15
20
25
30
35
40
45
0
5
10
15
20
25
30
0
10
20
30
40
50
60
70
0
20
40
60
80
100
120
0
20
40
60
80
100
120
140
160
0
50
100
150
200
250
300

Figure 4. Correlation between COD total and theoretical methane yield for different dilution volumes: (a) 1 L; (b) 1.5 L; (c) 2 L

The theoretical methane yield was calculated using the COD total in each dilution volume. From fig. 4, it can be seen that high COD contents obtained high methane yields for all dilution volumes. The dilution volume of 2 L got the most methane yield of 264.70 mL/gVS on day 16, followed by dilution volumes of 1.5 L and 1 L with the highest methane yields of 92.02 mL/gVS and 24.41 mL/gVS, respectively. The lowest methane yield was obtained at the lowest COD total for all dilution volumes. From the results, it can be inferred that the COD total affected theoretical methane yields. The statistical analysis also proved the significant impact of COD total towards the theoretical methane yield with a p-value of 0.013 ($p < 0.05$). Tang et al. [26] obtained a methane yield of 276 ± 34 mL/gVS for the digestion of mustard residuals. Yan et al.[27] reported cauliflower residues generated a methane yield of 249.61 mL/gVS. Czubaszek et al.[28] found the highest methane yield of 297.81 ± 0.65 L/kgVS during the anaerobic digestion of cabbage leaves. Compared to the previous literature, the theoretical methane yield obtained in this study is almost close to the experimental methane yield obtained by the anaerobic digestion of mustard residuals, with a yield difference of 4.27%.

Conclusions

This study investigated the effect of different dilution volumes on biogas production and the correlation between dilution volumes and theoretical methane yield. The results showed that the modified Gompertz model is the best-fit model for anaerobic digestion of green mustard residuals with R^2 of 0.9992-0.9995. Dilution volumes significantly affect biogas production ($p < 0.05$). The highest cumulative yeast of 4372.58 mL/gVS was obtained at a dilution volume of 2 L. The dilution volume significantly correlates with theoretical methane yield ($P<0.05$).

Acknowledgements

We thank all persons who had any contributions to this research.

Conflict of Interest

The authors declare no conflict of interest

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Modified Gompertz	$M_t = M_0 \times exp\{-exp[(R_m.e/M_0) \times (\lambda - t) + 1]\}$	[17]

Table 2. Kinetic parameters of first-order, Fitzhugh, and modified Gompertz models

		Dilution volumes		
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	k (1/day)	0.096	0.092	0.084
	n	3.00	3.00	3.00
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List of Figures

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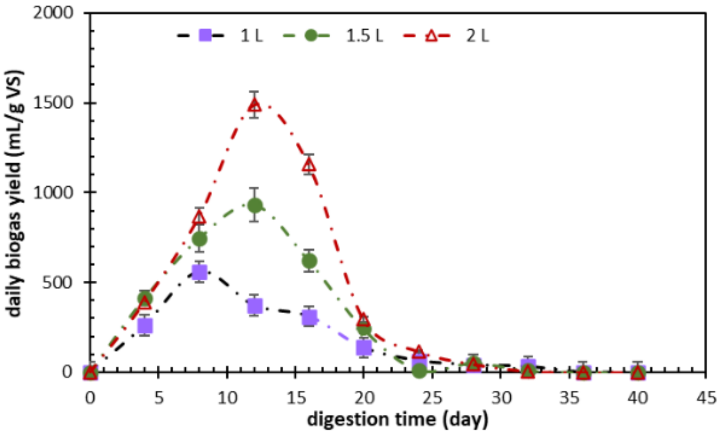


Figure 2. Cumulative biogas yields during anaerobic digestion of mustard green wastes.

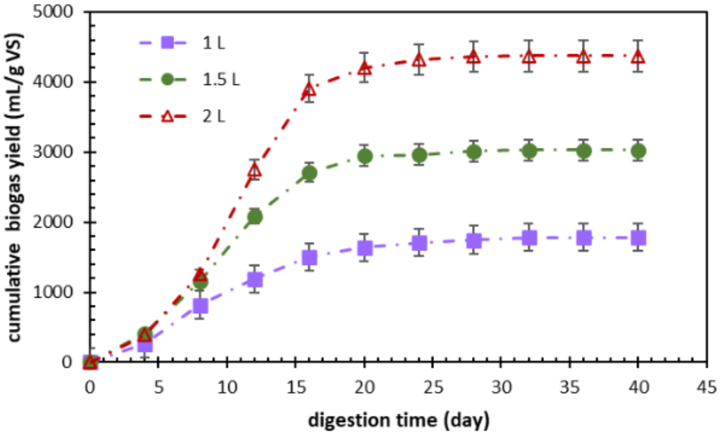
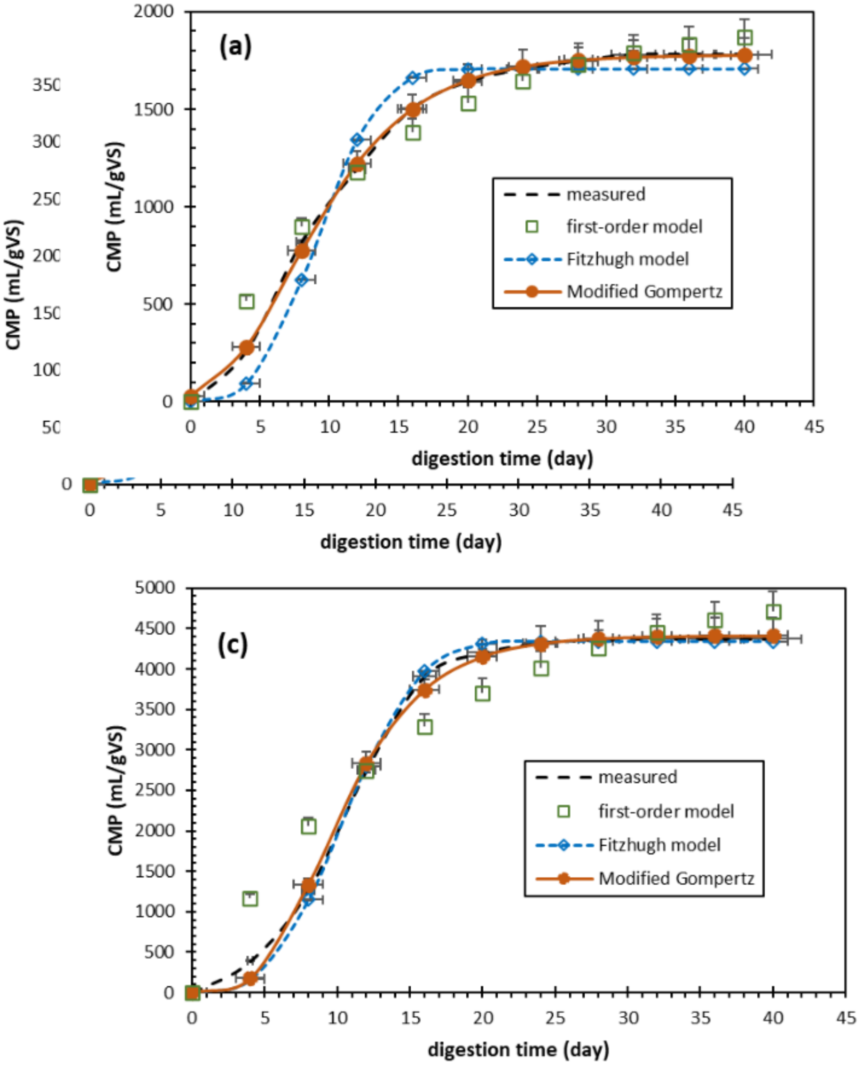


Figure 3. Regression fitting of cumulative biogas yield following first-order, Fitzhugh, and modified Gompertz models in different dilution volumes: (a) 1 L; (b) 1.5 L; (c) 2 L



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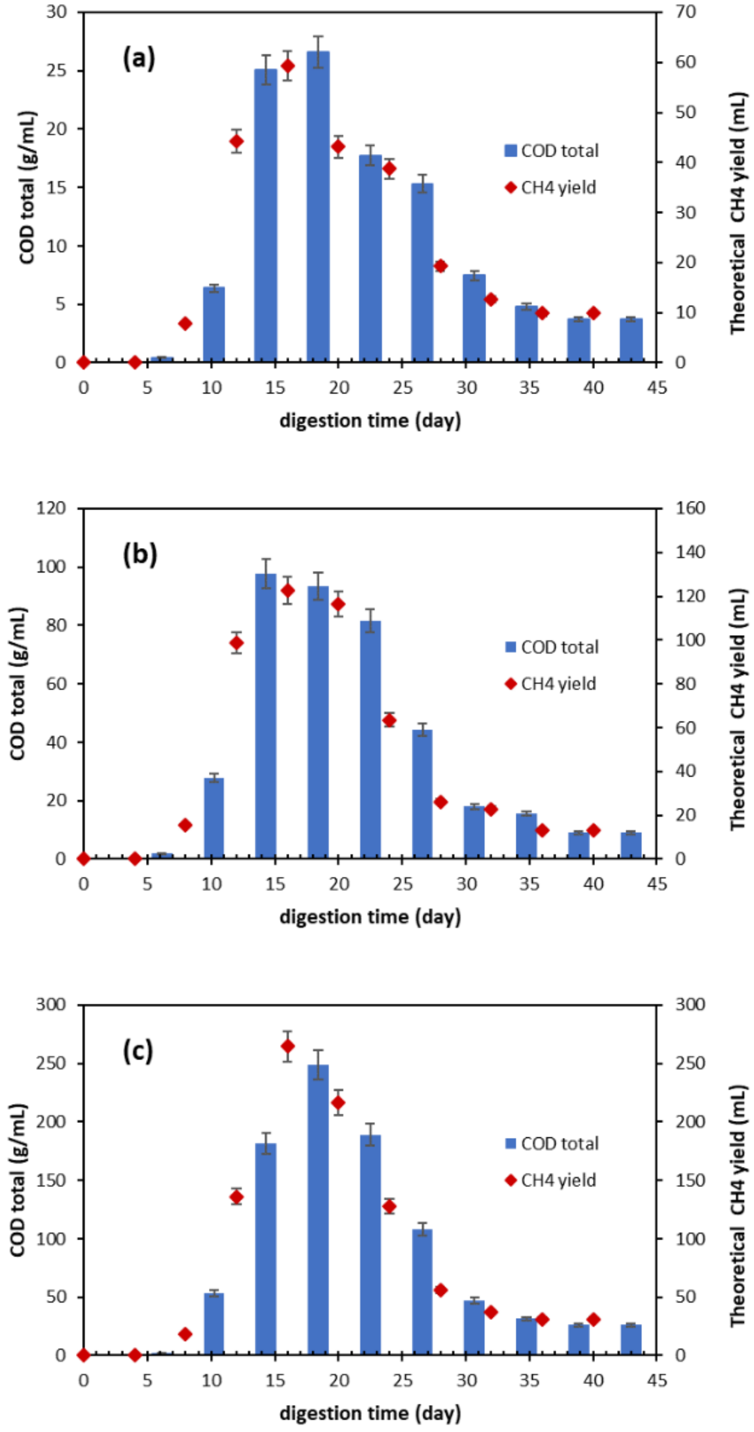
(a)
COD total (g/mL)
0
5
10
15
20
25
30
Theoretical CH4 yield (mL)
0
10
20
30
40
50
60
70
COD total
CH4 yield
digestion time (day)
0
5
10
15
20
25
30
35
40
45
(b)
COD total (g/mL)
0
20
40
60
80
100
120
Theoretical CH4 yield (mL)
0
20
40
60
80
100
120
140
160
COD total
CH4 yield
digestion time (day)
(c)
COD total (g/mL)
0
50
100
150
200
250
300
Theoretical CH4 yield (mL)
0
50
100
150
200
250
300
COD total
CH4 yield
digestion time (day)

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