Kinetic Modeling of Biomethane Production from Cassava Peel Waste: Impact of Silica Gel as an Adsorbent

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Abstract: *This study investigates the role of silica gel as an adsorbent in enhancing biomethane generation during anaerobic digestion of cassava peel waste. Cassava peel, a carbohydrate-rich agricultural byproduct, is widely available but often discarded, creating environmental concerns. Although suitable for biogas production, the methane fraction is often reduced by the presence of CO_2 and moisture. In this work, laboratory-scale fixed-bed bioreactors were operated at different inoculum-to-water ratios (100:0, 70:30, 60:40, and 50:50 v/v) with and without silica gel. The digestion process was monitored for 22 days by measuring total suspended solids (TSS), pH, and cumulative biomethane production. Silica gel was placed in the reactor headspace to adsorb CO_2 and water vapor, resulting in a gradual decrease in TSS, indicating organic matter degradation, while pH remained within the optimal range for methanogenesis. Biomethane production varied with the inoculum ratio, and silica gel accelerated the attainment of peak yield at the 100:0 ratio. Kinetic analysis showed that the modified Gompertz model best described the experimental data. These results demonstrate the potential of silica gel as a cost-effective adsorbent to improve biomethane quality and enhance the efficiency of small-scale anaerobic digestion systems.*

Keywords: *adsorbent; anaerobic digestion; cassava peel; silica gel; biomethane; kinetic modeling*

■ INTRODUCTION

The global reliance on fossil fuels, which currently supply nearly 88% of total energy demand, underscores the urgent need to accelerate the adoption of renewable alternatives [1]. Among the options, biogas is increasingly valued as a decentralized, low-cost energy source that supports both energy security and waste reduction initiatives. Its utilization not only contributes to sustainable power generation but also minimizes the environmental burden from unmanaged organic residues [2]. Biogas is generated through anaerobic digestion, a multi-step microbial process involving hydrolysis, acidogenesis, acetogenesis, and methanogenesis [3-4]. During these stages, complex organic macromolecules such as carbohydrates, proteins, and lipids are progressively degraded by microbial consortia. While this process is considered energy-efficient and environmentally friendly, its efficiency is influenced by substrate type, operating conditions, and microbial stability [2].

Cassava (*Manihot esculenta*) is extensively cultivated in Indonesia, producing large amounts of peel waste (10–20% of total tuber weight) that is typically discarded [5]. Due to its high carbohydrate content, cassava peel is a promising substrate for biogas production. Previous studies demonstrated that cassava peel digestion could yield significant amounts of biogas; for example, Okudoh et al. [5] obtained methane concentrations of 51% in mesophilic systems while Anyanwu et al. [6] reported methane yields of 0.6 L/kg TS. However, the relatively low methane content limits its direct use as a fuel, requiring upgrading. Recent studies emphasize that the inoculum-to-substrate ratio is a critical factor influencing anaerobic digestion efficiency. This ratio affects microbial activity, lag phase duration, and biogas yield [2]. A higher inoculum fraction can accelerate methanogenesis and stabilize the process, whereas excessive dilution may reduce substrate availability. Thus, optimizing the inoculum-to-water ratio is essential for maximizing biogas output.

In parallel, gas purification using adsorbents has emerged as a practical upgrading method. Silica gel, due to its high surface area and affinity for water vapor and CO_2, has shown promise as a low-cost adsorbent. Studies reported its effectiveness in biogas drying and methane enrichment, although its selectivity is lower than that of activated carbon, zeolites, or biochar [7-9]. Adsorption equilibrium studies of biogas components on silica gel have demonstrated a clear selectivity sequence of $H_2O > CO_2 > CH_4$ over a wide range of pressures and temperatures [7]. The strong affinity toward water vapor arises from the hydrophilic and polar surface of silica gel dominated by silanol (Si–OH) groups, while the quadrupolar nature of CO_2 enables moderate interactions with the silica surface [10]. In contrast, the interaction of non-polar CH_4 with the polar silica gel surface is much weaker, resulting in significantly lower CH_4 uptake. Although methane adsorption is not negligible, its adsorption capacity is substantially lower than that of CO_2 and H_2O [9], supporting the use of silica gel as a selective adsorbent for water and CO_2 removal during biogas upgrading.

Silica-based materials derived from biomass residues have also attracted considerable attention due to their high silica content and functional properties for catalytic and adsorption applications, as demonstrated by the extraction of silica from sugarcane bagasse ash for the synthesis of SiO_2-based composite materials [11]. Despite growing interest in adsorbent-assisted biogas upgrading, the application of silica gel as an *in-situ* CO_2 scavenger in cassava peel digestion, particularly in relation to the inoculum-to-water ratio and kinetic modeling, has not been sufficiently explored.

This research, therefore, focuses on the combined effects of inoculum-to-water ratios and silica gel addition on cassava peel digestion. The objectives are: (i) to examine the influence of silica gel on TSS and pH, and biomethane yield, (ii) to evaluate methane enrichment through the flame test, and (iii) to determine the most suitable kinetic model (Cone, Logistic, or modified Gompertz) to describe the biogas production trend.

■ EXPERIMENTAL SECTION

Materials

Cassava peels were collected from local markets in Medan, Indonesia. The peels were separated from the outer epidermis, washed with distilled water, chopped, and blended without additional water to form a fine substrate. The inoculum was obtained from the up-flow anaerobic sludge blanket (UASB) unit of a domestic wastewater treatment facility (*Perumda Tirtanadi*, Medan). Synthetic silica gel beads were used as adsorbents due to their high surface area and hydrophilic properties. Silica gel, as a silica-based porous adsorbent, is characterized by a high specific surface area (typically above 500 m^2/g), pore sizes ranging from 1 to 100 nm, and porosity above 80%, which contribute to its excellent adsorption performance for moisture and gaseous compounds [12].

Instrumentation

Anaerobic digestion was performed in a 50 L laboratory-scale fixed-bed bioreactor. Each bioreactor was equipped with a gas outlet connected to a U-tube manometer for monitoring biogas production, a thermometer for temperature monitoring, and a sampling port for periodic collection of liquid samples. In addition, a compartment containing silica gel was installed in the headspace to interact with the produced gas without direct contact with the slurry. The reactors were loaded with approximately 40 L of substrate mixture, leaving sufficient headspace for gas accumulation. A schematic diagram of the laboratory-scale anaerobic bioreactor used in this study is presented in Fig. 1.

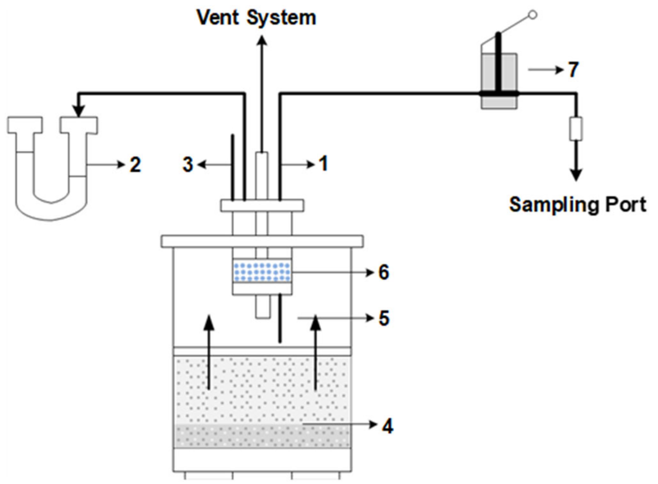

Fig 1. Schematic diagram of laboratory-scale fixed-bed anaerobic bioreactor: (1) sampling port, (2) U-tube manometer, (3) thermometer, (4) substrate mixture, (5) water vapor and gas mixture, (6) silica gel compartment, and (7) head pump

Procedure

The substrate mixture was prepared to maintain a total solids (TS) concentration of 7–9%. The bioreactors were operated at four different inoculum-to-water ratios: 100:0, 70:30, 60:40, and 50:50 (v/v). For each condition, 3 kg of cassava peel slurry was mixed with the designated proportions of inoculum and water. Two sets of reactors were employed in this study. Set I (A1–A4) consisted of reactors equipped with silica gel placed in the headspace compartment, whereas set II (A5–A8) served as the control group without silica gel.

All reactors were operated under mesophilic conditions (28–32 °C) for 22 days. In the silica gel-assisted systems (A1–A4), the adsorbent was positioned in a perforated container inside the reactor headspace, allowing the produced gas to pass through the silica gel bed. This configuration facilitated the adsorption of moisture and partial CO_2 before the gas exited through the outlet.

Total suspended solids (TSS) and pH were measured every two days according to APHA (2005) standard methods [13]. Biogas production was estimated based on the difference in water height in the U-tube manometer. The flame test was conducted at the end of the digestion process by channeling the produced gas through a hose to a laboratory burner and observing the flame color. The presence of biomethane was confirmed by the appearance of a stable blue flame.

RESULTS AND DISCUSSION

Performance of Anaerobic Digestion of Cassava Peel Waste

Performance of anaerobic digestion in this study is indicated by TSS and pH. The TSS expressed the number of suspended particles on the substrate, i.e., solids retained on the filter paper during the test treatment. A high TSS value indicates substrate turbidity, which can affect biogas production. TSS was also used in this study to assess the performance of a silica gel fixed-bed reactor at different inoculum-to-water ratios and digestion times.

Fig. 2 illustrates the variation in TSS concentration across all bioreactors (A1–A4). These correspond to reactors containing silica gel with inoculum proportions of 100, 70, 60, and 50%, respectively. In general, TSS levels declined as digestion progressed, indicating continuous breakdown of suspended organic solids. On day 4, the reduction rates of organic matter in A1–A4 reached 40.22, 42.05, 52.33, and 56.55%, respectively. Systems with higher inoculum fractions and elevated organic loading appeared to suppress microbial growth due to limited nutrient availability, thereby lowering biogas production.

Cassava peel is rich in starch and biodegradable organic matter, which can support microbial activity during anaerobic digestion [14]. Pandia et al. [15] emphasized that in batch anaerobic digestion, prolonged

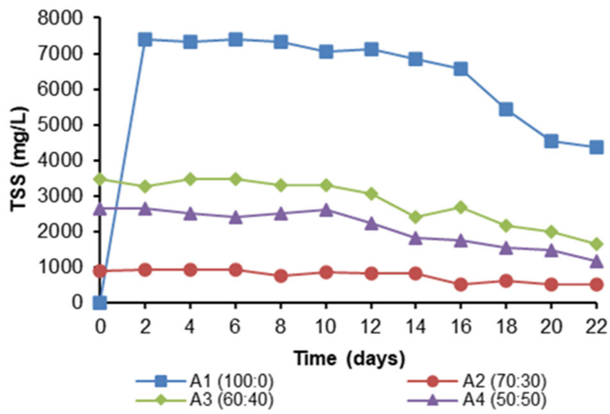

Fig 2. TSS profile during the digestion of cassava peel waste

retention times generally enhance TSS removal, although the optimum level depends on both the substrate mixture ratio and the initial TSS concentration. Since the initial TSS concentration strongly correlates with removal efficiency, wastewater characteristics and pre-treatment approaches are crucial factors influencing the extent of TSS reduction [16]. Furthermore, the efficiency of TSS removal is governed not only by anaerobic microbial activity but also by physicochemical reactions occurring within the waste biomass [17]. Collectively, these results suggest that incorporating silica gel in fixed-bed bioreactors provides a favorable environment for reducing TSS during biomethane production.

The stability of anaerobic digestion is strongly influenced by pH [17], which reflects the system's acidity or alkalinity. Methanogenic microorganisms thrive under neutral to slightly alkaline conditions. Fig. 3 presents the pH variations in each bioreactor during the experimental period. A decline in pH during the initial stage of digestion indicated the occurrence of hydrolysis and acidogenesis. At this stage, enzymes and hydrolytic microbes decompose the cassava peel substrate by breaking down complex polysaccharides and cellulose into simpler sugars. These sugars are subsequently fermented through acidogenesis to form volatile fatty acids, hydrogen, CO_2, and acetic acid, which are later utilized by methanogens to produce methane.

The measured pH values throughout 22 days of operation ranged from 5.59 to 7.68 in bioreactor A1, 5.64 to 7.66 in A2, 5.66 to 7.68 in A3, and 5.78 to 7.77 in A4. Biomethane production was optimal at near-neutral pH (6.7–7.5), consistent with previous studies on methanogenic activity [18]. In general, the most favorable pH range for biogas generation is 6.5–7.5. Stabilization can be achieved by adding chemical buffers such as NaOH, KOH, $NaHCO_3$, or $Ca(OH)_2$ to cassava peel substrates [19].

The relatively stable near-neutral pH observed during fermentation suggests that silica gel did not significantly disturb the acid–base balance, consistent with previous studies reporting stable anaerobic digestion performance in the presence of silica-based carrier materials [20]. Overall, pH measurements confirmed that

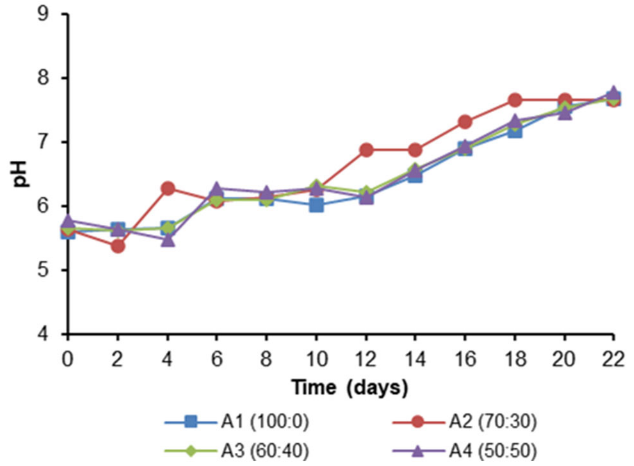

Fig 3. pH profile during the digestion of cassava peel waste

reactors supplemented with silica gel were still capable of maintaining an environment conducive to anaerobic digestion.

Effect of Silica Gel Media on Biomethane Yield

The volume of biomethane was estimated from the pressure generated by gas accumulation inside the digester, which displaced the water level in the U-tube manometer. The difference in water height was measured manually and converted to gas volume, while the flame test was applied to confirm the presence of methane. In this study, silica gel functioned both as an adsorbent, capturing moisture from the produced biogas, and as a medium that indirectly supported microbial activity. The cumulative biogas production patterns are presented in Fig. 4. Bioreactors A1–A4 were supplemented with silica gel at inoculum-to-water ratios of 100:0, 70:30, 60:40, and 50:50, respectively, while bioreactors A5–A8 served as controls without silica gel under the same inoculum conditions.

At the 100:0 ratio, bioreactor A1 achieved peak yield on day 14 (130.83 mL/g), after which production declined. By comparison, bioreactor A5 continued to increase until day 20, reaching 138.53 mL/g. This suggests that silica gel accelerated the attainment of maximum yield, but its effect diminished afterward, likely due to saturation or desorption. A similar trend was observed in the 70:30 ratio: bioreactor A2 reached a maximum yield on day 16 (49.06 mL/g), then declined,

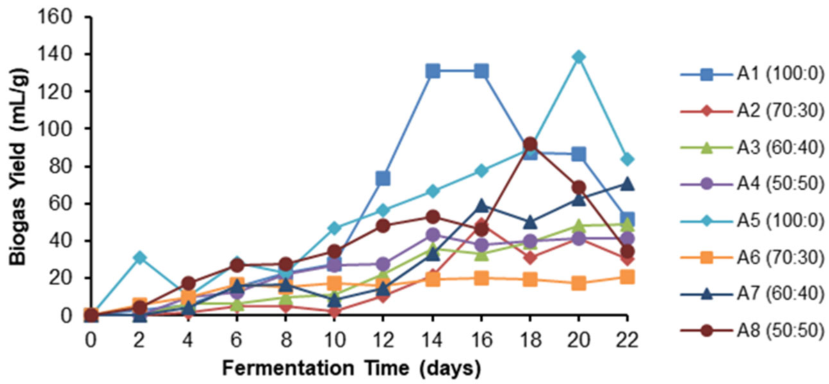

Fig 4. Cumulative biomethane production in bioreactors with and without silica gel at different inoculum-to-water ratios

whereas bioreactor A6 fluctuated and peaked on day 22 (20.66 mL/g). At the 60:40 ratio, the reactors without silica gel performed better, with bioreactor A3 (with silica gel) producing only 49.06 mL/g on day 22, compared to 70.65 mL/g from A7. At the 50:50 ratio, bioreactor A4 displayed stable performance, peaking on day 14 (43.18 mL/g), while bioreactor A8 reached a higher yield on day 18 (92.35 mL/g) before decreasing sharply.

During the early stage (0–6 days), gas yields were generally low across treatments, except in bioreactor A5, which showed a rapid increase from day 2 (31.40 mL/g). In the mid-stage (8–16 days), most reactors reached their maximum production, particularly A1, A2, and A4. In the late phase (18–22 days), gas yields declined across nearly all systems, reflecting substrate depletion or reverse reactions. These findings highlight that while silica gel can enhance gas release by adsorption, its limited capacity results in a plateau or decline once saturation occurs. In some cases, its use may even reduce yields, as observed in A2 versus A6, and A3 versus A7, possibly due to mismatched adsorption capacity and substrate availability. Overall, the yield trends demonstrate a nonlinear kinetic behavior.

Comparable observations were reported in previous studies. Salam et al. [8] examined mesophilic anaerobic digestion of cow dung using silica gel and noted an 11.94% increase in gas yield. Similarly, Ahamed et al. found that adding silica gel to poultry and household waste digestion systems enhanced total biogas production by 33.12%. The authors attributed this improvement to the adsorbent's surface properties, which concentrate substrates locally, thereby creating microenvironments that favor microbial growth and activity [9].

The addition of silica gel was initially expected to improve biogas upgrading efficiency by enhancing the combustion quality of the upgraded gas. However, the findings of this study did not support that assumption. Under mesophilic conditions, the use of adsorbents may even reduce process efficiency, either by unintentionally trapping microorganisms—thereby limiting their access to the substrate—or by adsorbing part of the produced biogas and restricting its release. In contrast, thermophilic systems have shown better outcomes when adsorbents are applied, indicating that operational temperature plays an important role [21].

Several other factors also contribute to limited biogas formation in bioreactors. Microbial degradation efficiency depends on both the type of organic substrate and the duration of digestion. Cassava peel, while rich in organic carbon, requires sufficient microbial cell development before methane can be produced. Silica gel relies on weak van der Waals interactions for adsorption, which are not strong enough to achieve effective biogas upgrading. Consequently, its adsorption capacity is lower than that of other adsorbents, such as zeolites or activated carbon, which possess larger surface areas and higher affinity for gas molecules [22].

The flame test served as a simple qualitative indicator for methane presence. As shown in Fig. 5(a) and (b), bioreactors A1 and A4 (with silica gel) produced a blue flame, confirming the presence of methane, whereas the gas from A2 and A3 failed to ignite. This can be attributed to the relatively low CO_2 selectivity of silica

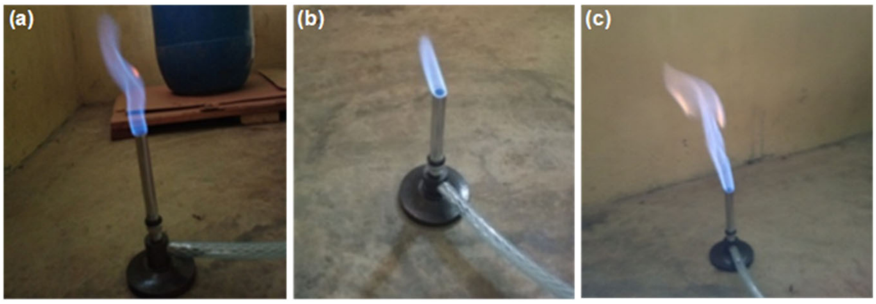

Fig 5. Flame test on gas from bioreactor (a) A1 (100:0), (b) A4 (50: 50) with silica gel, and (c) A5 (100:0) without silica gel

gel compared to activated carbon. Although silica gel can adsorb some CO_2, its efficiency is insufficient to substantially alter the methane-to-CO_2 ratio. The adsorption isotherms for CO_2 on silica gel demonstrate a shallow slope, indicating limited capture under typical biogas conditions [7]. Since the CO_2 fraction strongly influences combustion, higher concentrations make ignition more difficult and reduce flame stability. Consequently, the elevated CO_2 content in raw biogas not only lowers its combustion performance but also diminishes its economic value as a renewable fuel [23].

Flame tests were also performed on the gas generated from reactors without silica gel. As illustrated in Fig. 5(c), only the gas from bioreactor A5 successfully produced a visible flame, while no ignition was observed for A6, A7, or A8. The occurrence of combustion indicates the presence of methane, confirming that biogas was formed in measurable amounts [23]. Among the control systems, A5 achieved the highest gas yield, which explains its ability to sustain a flame compared to the other reactors.

Overall, reactors containing silica gel produced greater volumes of combustible gas than those without it, as the adsorbent contributed to partial CO_2 removal, thereby enriching the methane content. A previous study showed that CO_2 adsorption on silica gel can be described by the Langmuir and the Freundlich isotherm models, with high correlation coefficients ($R^2 \approx 0.998–0.999$), confirming its ability to adsorb CO_2 molecules. The Freundlich constant ($n < 1$) indicates possible chemisorption interactions between CO_2 and silanol groups on the silica surface. In addition, adsorption performance is strongly influenced by operating conditions: higher pressures enhance CO_2 uptake, while elevated temperatures reduce adsorption due to the exothermic nature of the process. Therefore, under near-atmospheric pressure typical of anaerobic digestion systems, silica gel mainly acts as a moderate CO_2 scavenger rather than a high-capacity separation material [10]. In contrast, biogas from reactors without silica gel had higher CO_2 concentrations, reducing its flammability. These findings reinforce the notion that elevated CO_2 levels hinder ignition and lower fuel quality.

Although this study confirmed the potential of cassava peel as a feedstock for biomethane, the relatively weak adsorption efficiency of silica gel limits its effectiveness as an upgrading agent. CO_2 adsorption commonly uses porous materials such as zeolites, activated carbon, and silica gel, which capture CO_2 via physisorption or chemisorption. Zeolite 13× exhibits high adsorption capacity but is sensitive to moisture, whereas activated carbon offers easier regeneration and stable performance over repeated cycles. Amine-functionalized silica gel can further improve CO_2 selectivity. More recently, advanced materials such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) have attracted increasing attention due to their tunable pore structures, large surface areas, and high chemical and thermal stability, making them promising candidates for efficient CO_2 capture [24].

A comparative study on adsorption using silica gel and activated carbon conducted by Danish et al. [25] demonstrated that activated carbon exhibits significantly higher adsorption capacity and better column efficiency than silica gel under identical conditions. The CO_2 adsorption capacity of silica gel was reported to be 8.61 mg/g at 298 K, whereas that of activated carbon was

73.1 mg/g. This substantial difference indicates that although silica gel can serve as a low-cost adsorbent, its adsorption performance is considerably lower than that of more selective, high-surface-area materials such as activated carbon. Future investigations should focus on evaluating alternative adsorbents with greater selectivity under both mesophilic and thermophilic operating conditions to achieve more consistent improvements in methane quality.

Kinetic Evaluation of Biogas Production

The measurement of biogas volume was based on the pressure generated inside the digester, which displaced the water level in the U-shaped manometer. The height difference was recorded manually, and the corresponding volume was calculated from the number of gas moles. To evaluate production kinetics, three commonly applied models—Cone, modified Gompertz, and Logistic—were employed to compare the performance of reactors operated with and without silica gel across four inoculum-to-water ratios.

Model performance was assessed using two statistical indicators: the coefficient of determination (R^2) and the root mean square error (RMSE). R^2 represents the proportion of variance explained by the model; values approaching 1 indicate a stronger fit, and values above 0.9 are generally considered reliable. Conversely, lower RMSE values denote higher prediction accuracy. Together, these measures ensure that model predictions are both accurate and robust, demonstrating the model's capability to capture the dynamics of anaerobic digestion. By comparing these statistical parameters, the most appropriate model can be identified, providing valuable insight into biogas yield prediction and process understanding [26].

Cone Model

The Cone model, expressed in Eq. (1), is derived from first-order nonlinear kinetics and incorporates a shape factor (n) that allows it to represent asymmetric gas production patterns [27]. It is particularly effective for describing substrate degradation in systems where the rates of hydrolysis and fermentation change over time.

$$B(t) = B_{\infty}\left(1 - e^{-kt^{n}}\right) \quad (1)$$

The kinetic fitting results obtained using the Cone model are presented in Table 1, which lists the estimated parameters of biogas potential (B_{∞}), rate constant (k), and curve shape factor (n). In the reactors containing silica gel (A1–A4), the biogas potential (B_{∞}) ranged from 42.15 to 93.77 mL/g VS. Meanwhile, the shape factor n decreased from 2.96 in A1 to 1.93 in A4. The observed decline in n with increasing dilution indicates a trend toward more linear degradation behavior under lower substrate concentrations, likely due to improved dispersion of hydrolysis products and reduced accumulation of inhibitory intermediates.

The rate constant (k) in reactors supplemented with silica gel remained relatively low (0.001–0.012 day^{-1}), indicating a steady, well-regulated degradation process. In contrast, reactors without silica gel (A5–A8) displayed greater variability in both k and n values. For instance,

Table 1. Kinetic parameters of the cone model

Bioreactor	Inoculum-water ratio	B_{∞} (mL/g)	K (day^{-1})	n	R^2	Total error^2	RMSE
	with silica gel						
A1	100:0	93.77	0.0010	2.96	0.95	6472.87	23.23
A2	70:30	40.35	0.0010	2.59	0.98	680.61	7.53
A3	60:40	56.77	0.0015	2.34	0.96	105.82	2.97
A4	50:50	42.15	0.0120	1.93	0.98	85.22	2.66
	without silica gel						
A5	100:0	111.31	0.001	2.78	0.96	4195.69	18.70
A6	70:30	19.38	0.180	1.09	0.97	21.09	1.33
A7	60:40	117.54	0.001	2.22	1.00	590.32	7.01
A8	50:50	61.73	0.020	1.75	0.99	2126.43	13.31

in A6, k reached 0.18 day-1 while n dropped to 1.09, indicating irregular or overstimulated microbial activity, likely due to insufficient buffering against inhibitory compounds. Providing an adequate inoculum concentration strengthens microbial interactions, thereby enhancing the conversion of substrate into biogas. Nevertheless, both inoculum-to-substrate ratio and substrate characteristics are key determinants in anaerobic digestion efficiency. Providing sufficient inoculum not only shortens the lag phase of methanogenesis but also alleviates digester inhibition [28]. Thus, inoculum levels directly influence both the yield and methane content of the produced gas. The statistical evaluation showed strong model performance, with R^2 consistently ≥ 0.96, confirming that the Cone model reliably captured the overall production trend. However, omitting silica gel led to higher residual errors, suggesting reduced model precision in its absence.

Fig. 6 and 7 present the Cone model fitting results. As shown in Fig. 6, the model successfully replicated the gradual accumulation of biogas in reactors containing silica gel, with curves closely aligned with experimental observations across all dilution levels. The curve profiles shifted slightly with increasing water content, consistent with the lower n values and reduced nonlinearity in substrate degradation. By contrast, the fits for reactors without silica gel (Fig. 7) were less smooth, particularly at the start of digestion, where the model tended to underestimate early-stage gas generation. This variability points to unstable microbial performance in the absence of buffering, potentially due to pH fluctuations or accumulation of inhibitory metabolites. Despite these deviations, the model still provided a reasonable representation of overall degradation dynamics and accurately predicted final cumulative yields.

Modified Gompertz Model

Applying the modified Gompertz model provides valuable insight into system performance and biogas kinetics. This model, expressed in Eq. (2) [29], represents cumulative biogas production as a sigmoidal function defined by three parameters: the maximum biogas potential (B_0), the maximum production rate (R_m), and the lag phase duration (λ). Its formulation allows for

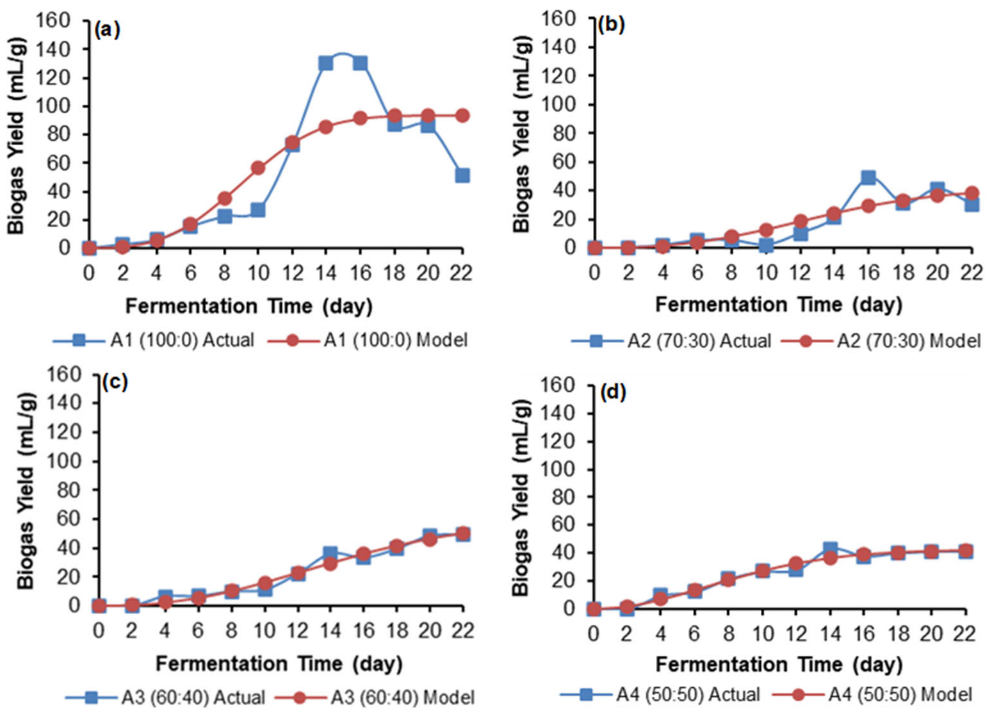

Fig 6. Cone model fitting curves for cumulative biogas production in bioreactors with silica gel at different mixing ratios: (a) 100:0, (b) 70:30, (c) 60:40, and (d) 50:50

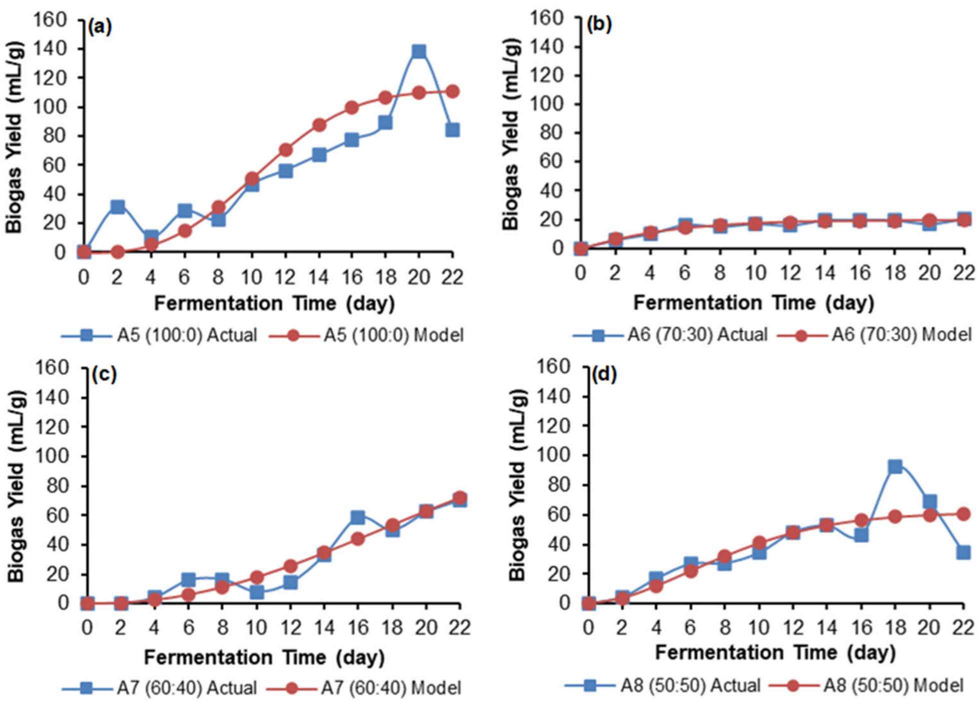

Fig 7. Cone model fitting curves for cumulative biogas production in bioreactors without silica gel at different mixing ratios: (a) 100:0, (b) 70:30, (c) 60:40, and (d) 50:50

accurate characterization of microbial growth dynamics, particularly capturing both the initial adaptation (lag phase) and the exponential production phase. Previous studies have also demonstrated that kinetic models, such as the modified Gompertz model, can effectively describe methane production behavior and the biogas generation potential during anaerobic digestion of organic waste substrates [30].

$$B(t) = B_0 \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{B_0} \cdot (\lambda - t) + 1\right]\right\} \quad (2)$$

The kinetic fitting results obtained with the modified Gompertz model are summarized in Table 2. In reactors containing silica gel (A1–A4), the lag phase consistently shortened with greater dilution, decreasing from 11.25 days in A2 (70:30 inoculum-to-water ratio) to only 2.40 days in A4 (50:50). This trend suggests that higher dilution in the presence of silica gel enhances microbial adaptation, likely due to reduced initial substrate concentrations and improved mitigation of inhibitory effects. Under high microbial density, inhibitory compounds such as volatile

Table 2. Kinetic parameters of the modified Gompertz model

Bioreactor	Inoculum-water ratio	B_0 (mL/g)	R_m (mL/g day)	λ (day)	R^2	Total error^2	RMSE
	with silica gel						
A1	100:0	178.02	20.07	8.11	0.94	917.97	46.92
A2	70:30	37.44	10.93	11.25	0.87	396.73	5.75
A3	60:40	65.67	3.34	5.21	0.99	103.60	2.94
A4	50:50	43.81	3.72	2.40	0.98	88.82	2.72
	without silica gel						
A5	100:0	162.81	5.89	2.25	1.00	2770.04	15.19
A6	70:30	18.41	2.89	0.16	0.96	20.28	1.45
A7	60:40	135.27	4.90	7.08	1.00	572.22	6.91
A8	50:50	63.61	4.97	1.43	0.99	2145.06	13.37

fatty acids (VFAs) and ammonia tend to accumulate, negatively affecting methanogenesis. Dilution reduces the overall concentration of these inhibitors, thereby allowing certain microbial groups to persist and outcompete others. Elevated ammonia levels, in particular, can suppress methanogenic activity, leading to VFA accumulation and reduced methane yields [31].

The highest biogas potential (B_0 = 178.0 mL/g VS) was obtained in reactor A1 (100% inoculum with silica gel). However, this condition was also associated with an extended lag phase, suggesting that excessive inoculum loading may initially hinder microbial activity due to ammonia or volatile fatty acid (VFA) accumulation. In comparison, reactors without silica gel (A5–A8) exhibited more inconsistent lag times, such as λ = 0.16 days in A6 and λ = 7.9 days in A7, reflecting instability in microbial growth kinetics. Although the treatments without silica gel produced high R^2 values (up to 1.00), these results were not always accompanied by low residual errors. This outcome highlights the importance of evaluating both statistical accuracy and biological plausibility when validating model predictions. Overall, while the modified Gompertz model provides a strong structural framework for describing biogas kinetics, its reliability is enhanced under stable environmental conditions, such as those facilitated by adsorbents.

Fig. 8 and 9 illustrate the cumulative biogas production predicted by the modified Gompertz model for reactors with and without silica gel. In reactors supplemented with silica gel (A1–A4), the curves displayed a characteristic sigmoidal trend, marked by a short adaptation phase, followed by a clear exponential increase and eventual stabilization. The model predictions aligned closely with experimental data, particularly in A3 and A4, where only minimal deviations were observed (R^2 > 0.98), confirming the high accuracy and consistency of the fit. In contrast, reactors lacking silica gel (A5–A8) produced more irregular profiles. Although the model generally followed the observed trends, particularly in A5 and A7, greater discrepancies occurred at the early stages and during the transition toward the stationary phase. These deviations likely reflect unstable microbial activity or accumulation of inhibitory compounds in the absence of adsorbent, leading to fluctuating gas production rates. The presence of adsorbents helps mitigate such effects by adsorbing VFAs, ammonia, and other inhibitory

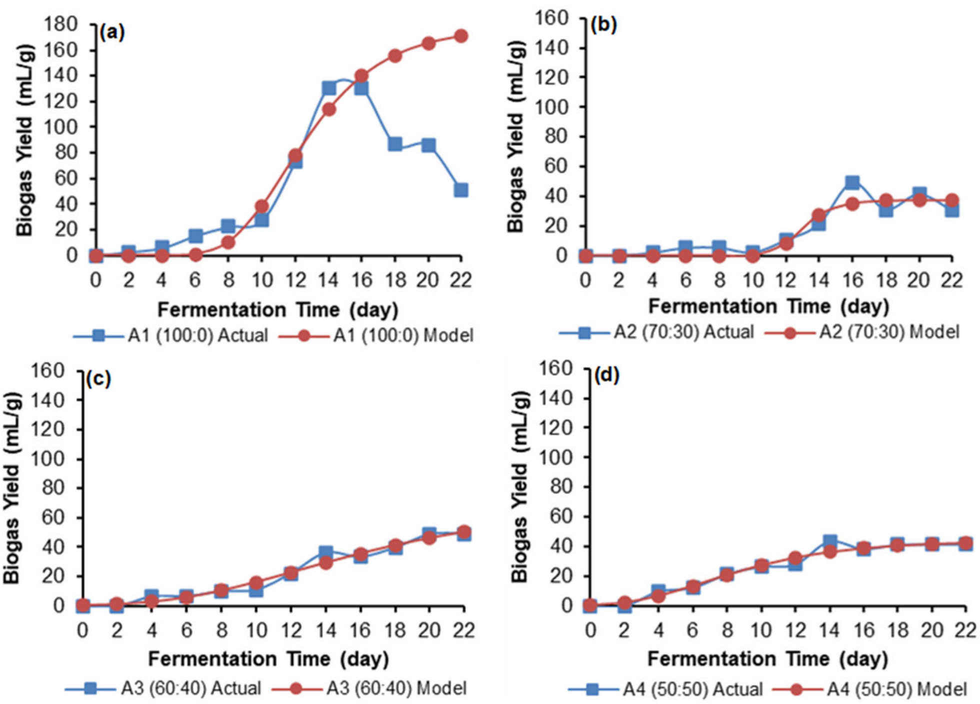

Fig 8. Modified Gompertz model fitting curves for cumulative biogas production in bioreactors with silica gel at different mixing ratios: (a) 100:0, (b) 70:30, (c) 60:40, and (d) 50:50

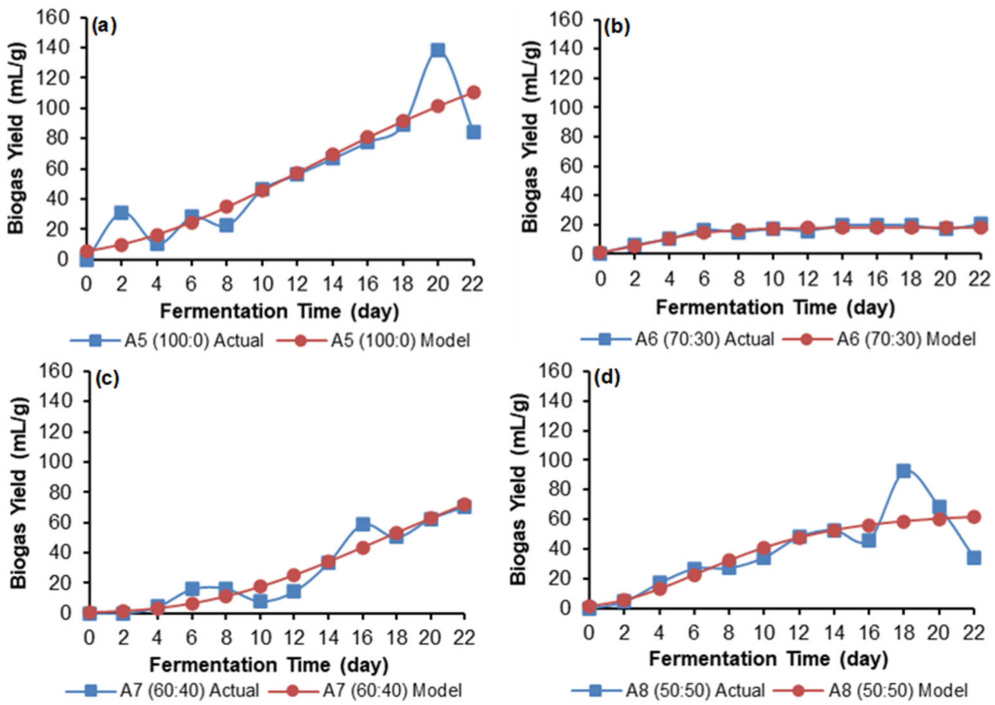

Fig 9. Modified Gompertz model fitting curves for cumulative biogas production in bioreactors without silica gel at different mixing ratios: (a) 100:0, (b) 70:30, (c) 60:40, and (d) 50:50

Table 3. Kinetic parameters of the logistic model

Bioreactor	Inoculum-water ratio	B_∞ (mL/g)	R_m (mL/g day)	λ (day)	R^2	Total error^2	RMSE
	with silica gel						
A1	100:0	96.51	26.93	8.85	0.85	5403.05	21.22
A2	70:30	37.63	10.20	11.40	0.87	367.22	5.53
A3	60:40	52.59	3.82	6.23	0.98	97.06	2.84
A4	50:50	41.59	3.86	2.89	0.97	97.32	2.85
	without silica gel						
A5	100:0	123.01	6.70	3.54	0.99	2614.79	14.76
A6	70:30	18.51	2.84	0.33	0.96	29.66	1.57
A7	60:40	79.62	5.64	7.93	0.99	516.34	6.56
A8	50:50	61.89	4.98	1.95	0.98	2118.61	13.29

substances, thereby lowering their concentrations in the digester and stabilizing microbial performance [32]. Despite these differences, the modified Gompertz model successfully captured the key kinetic phases of the digestion process under both conditions.

Logistic Model

The Logistic model, presented in Eq. (3), was applied to simulate cumulative biogas production as a symmetrical sigmoidal curve. This model is defined by three principal parameters: the maximum biogas potential (B_∞), the maximum production rate (R_m), and the lag phase duration (λ), which together represent microbial growth and gas accumulation over time [26]. The estimated parameters obtained from the Logistic model are summarized in Table 3.

$$B(t) = \frac{B_\infty}{1 + \exp\left(\frac{4R_m}{B_\infty}(\lambda - t) + 2\right)} \quad (3)$$

For reactors containing silica gel (A1–A4), the predicted B_∞ ranged between 37.63 and 96.51 mL/g VS, accompanied by decreasing R_m values and variable λ values depending on dilution. For instance, λ was 11.4 days in A2 but decreased to 2.9 days in A4, indicating that silica gel reduced the lag phase at higher dilutions. In the control reactors without silica gel (A5–A8), the maximum B_∞ reached 123.0 mL/g VS at A5 (100% inoculum), while lag durations varied and R_m values remained moderate (2.6–6.7 mL/g·day). As inoculum concentration decreased, lag phase variability increased, though the exact mechanism remains unclear [33]. The differences may be linked to the presence of inhibitory compounds or environmental fluctuations, as diluted inoculum systems tend to be more sensitive to such disturbances.

Although the Logistic model achieved acceptable R^2 values (0.85–0.99), it often struggled to represent sharp transitions observed during digestion, particularly at the early and stationary phases. Consequently, while this model can provide a reasonable approximation of overall growth trends, it is less reliable for describing detailed microbial dynamics, especially under conditions of stress or inhibition. The Logistic model fitting results (Fig. 10 and 11) exhibited greater variability in accuracy than those of the Cone and modified Gompertz models. In reactors containing silica gel, the model approximated the sigmoidal biogas production curves reasonably well at intermediate dilution ratios (A2 and A3). However, in A1 and A4, it tended to either under- or overestimate gas production, particularly during the lag and transition phases. This outcome corresponds with the broader range of lag phase (λ) values and lower R^2 observed in certain treatments. In reactors without silica gel, the Logistic model appeared to oversimplify system dynamics. The predicted curves often diverged from the experimental data at both the initial and final stages, underestimating the early lag behavior and failing to adequately describe the slowdown as gas production approached the plateau. These discrepancies highlight the model's limited ability to capture rapid metabolic changes or inhibitory effects in systems without buffering.

Taken together, the kinetic analyses provide important insights into microbial activity and gas-generation dynamics across varying inoculum-to-water ratios, with or without silica gel. Among the three models, the modified Gompertz consistently delivered the most accurate and comprehensive fit, particularly in describing lag and exponential phases of digestion.

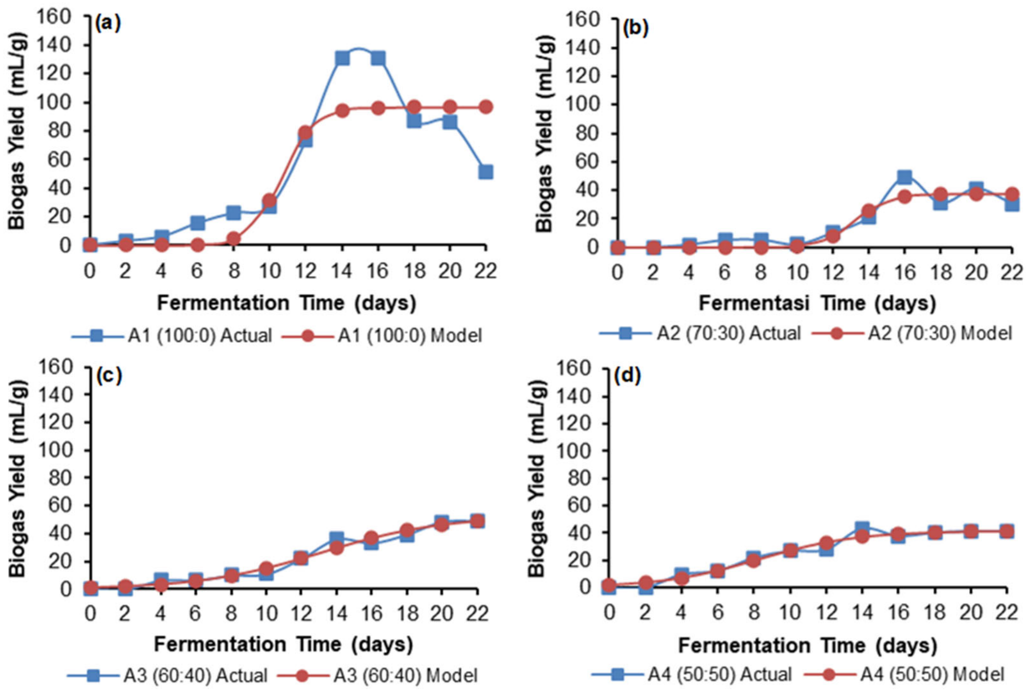

Fig 10. Logistic model fitting curves for cumulative biogas production in bioreactors with silica gel at different mixing ratios: (a) 100:0, (b) 70:30, (c) 60:40, and (d) 50:50

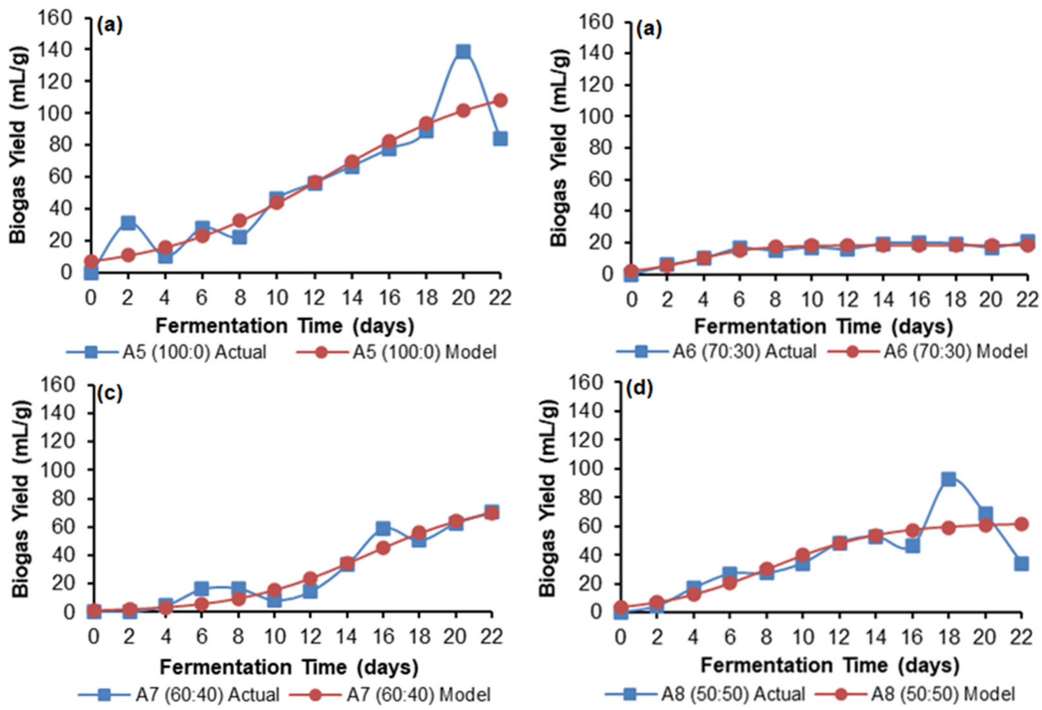

Fig 11. Logistic model fitting curves for cumulative biogas production in bioreactors without silica gel at different mixing ratios: (a) 100:0, (b) 70:30, (c) 60:40, and (d) 50:50

The Cone model effectively characterized substrate degradation behavior, while the Logistic model, although useful as a simplified representation of growth, proved less reliable under complex or unstable operating conditions.

■ CONCLUSION

This study evaluated the influence of silica gel as an adsorbent in fixed-bed anaerobic digestion systems for biomethane production from cassava peel waste. The decline in TSS followed similar patterns in reactors with and without silica gel, confirming effective organic matter degradation across treatments, while pH remained within the optimal range for methanogenesis and was not significantly affected by the addition of silica gel. Silica gel accelerates the attainment of the highest biomethane yield at the 100:0 ratio (130.83 mL/g on day 14), although a subsequent decline was observed. Flame test results showed that reactors with silica gel produced a stable blue flame at 100:0 and 50:50 ratios, whereas those without silica gel produced combustible biogas only at 100:0. This suggested that CO_2 adsorption by silica gel can enhance biogas combustibility despite its limited selectivity. The modified Gompertz model most accurately kinetic model described cumulative biogas production, particularly in reactors containing silica gel. Although silica gel accelerated early gas production, its relatively low selectivity and limited adsorption capacity limit its effectiveness for long-term upgrading. Therefore, future studies should focus on higher-performance adsorbents, such as zeolites or activated carbon, and assess their application under optimized mesophilic or thermophilic conditions.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Maya Sarah, Sunarti Abdul Rahman, Fatimah, Farida Hanum, Rivaldi Sidabutar, Ashwin Charles Benedict, and Malyanah Mohd. Taib were responsible for conceptualization and methodology. Maya Sarah and Eva Malini Simare-mare conducted the experimental work and data collection. Maya Sarah and Isti Madinah conducted data analysis and visualization and wrote and revised the manuscript. Maya Sarah, Sunarti Abdul Rahman, Fatimah, and Farida Hanum supervised the overall research activity. All authors agreed to the final version of this manuscript.

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