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Comparative Kinetic Modelling and Performance Evaluation of an Anaerobic Fixed-Bed Reactor Treatment of Dairy Sludge Waste: Effect of Immobilization Media Types

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Abstract

This study evaluates the performance of anaerobic fixed-bed reactors for treating dairy sludge waste using two different immobilizing media, i.e. natural zeolite and porous bioceramics. Kinetic modeling was performed using Monod, Contois, and Moser models to determine substrate degradation (sCOD) and methane production rate. The results indicated that for the zeolite media, the Moser model resulted in the best fit R^2 of 0.9287 and RMSE of 500.12 mg/L with an exponential constant (n) of 2.92, reflecting high microbial sensitivity and synergistic effects in the biofilm. In contrast, the bioceramics media demonstrated the highest statistical stability across all models, with the Monod and Moser models achieving an identical R^2 of 0.9939. However, a significant functional discrepancy was observed. While bioceramics provided superior statistical fitting, they failed to facilitate effective methanogenesis, with methane concentrations remaining below 10%. Zeolite, despite having a slightly lower statistical fit, achieved a peak methane concentration of 37.82% on day 6. This suggests that zeolite's considerable cation exchange capacity effectively mitigates ammonia inhibition from protein-rich dairy sludge, a factor not captured by simplified empirical deterministic kinetic models. This research emphasizes that statistical stability in kinetic modeling did not inherently correlate with bio-energy recovery efficiency, affirming the importance of media selection.

Keywords: anaerob; bioceramics; dairy sludge; kinetic modeling; zeolite

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INTRODUCTION

Dairy processing industry is an agricultural sector that continues to grow in line with increasing consumer demand for dairy-based food products. However, this activity produces large amounts of liquid waste (sludge) containing high concentrations of organic compounds such as protein, fat, and lactose. Without adequate treatment, the direct disposal of this waste into the environment can cause serious pollution of water bodies and soil, as identified by a significant decrease in dissolved oxygen (DO) levels, eutrophication, and disruption to aquatic life. Therefore, dairy industry waste management has become an important challenge in environmental protection and sustainable development efforts. Pirsaheb *et al*. (2019) reported that the addition of zeolite (5 g/L) in a baffled anaerobic digestion of sludge and corn silage increased biogas production by up to 70% and 22%, respectively. These results confirm the role of zeolite in enhancing biological surface area and ammonium binding. Meanwhile, a study on cassava waste showed that zeolite (3 g/L) produced a cumulative CH_4 of 653 mL/g VS, compared to 611 mL/g VS with biochar, and both were significantly higher than the control (Pirsaheb *et al*., 2019).

Biological treatment of waste through anaerobic processes has been popularly known as an efficient and environmentally friendly solution for decomposing organic matter in liquid waste. Anaerobic reactor systems are not only capable of reducing pollutant concentrations, but also possess a promising potential to produce renewable energy in the form of biogas. One of the widely preferred approaches in these issues is the use of fixed-bed reactors employing microbe's immobilizing media, which can increase the efficiency of the degradation process. Various kinetic modeling approaches have been proposed to model the anaerobic digestion process, particularly in predicting substrate degradation patterns and methane formation. The modified Gompertz model is one of the most widely applied models, specifically due to its ability to describe the lag phase, maximum methane production rate, and potential for cumulative gas accumulation. Research by Momodu and Adepoju (2021) revealed that the Gompertz and two-stage logistic models are more accurate in representing the dynamics of anaerobic systems than the first-order model, which is too simple to describe the complexity of the biological processes involved.

Other studies, such as comparative analysis of five kinetic models, also reinforce the superiority of the Gompertz model indicated by its high determination coefficients (R^2) and low prediction errors (RMSE). The logistic, Richards, and Cone models also demonstrate good performance, especially for complex substrates with sigmoidal characteristics. In some specific conditions, the Monod model remains relevant, particularly when the substrate-to-inoculum ratio is at its optimum value and the biomass data is available to calculate the growth rate of microorganisms. On the other hand, the Moser model can be a potential alternative to two-stage digestion systems. This model resulted in a lower relative error compared to the both Monod and Contois models, making it worth for application in systems involving multiple reaction pathways. These findings indicate that the selection of the appropriate kinetic model must be tailored to the substrate characteristics, reactor type, and parameters available from experimental data (Owhondah *et al.*, 2016).

Immobilization media play an important role in anaerobic reactor systems because they can provide a large surface area required for microorganism growth, increase contact between the substrate and biomass, and maintain microbial community stability. Various types of media, such as zeolite, plastic, and bioceramics, have been studied to determine their effectiveness in accelerating the biodegradation process. However, there is still a knowledge gap regarding the comparison of biogas production kinetic parameters among various types of immobilization media under uniform operating conditions, particularly in fixed-bed batch reactor systems. Currently, very few comprehensive studies have been carried out on the use of zeolite and bioceramic media in the context of dairy industry wastewater. However, Oliver *et al*. (2024) stated that bioplastic design affects the biogas rate, reaching up to 30 mL/g VS per day. This exhibites the potential of non-zeolite media with different pore characteristics and mechanical strength. The use of inorganic immobilization media, such as zeolite and bioceramics in anaerobic digestion systems has been proven effective in improving process efficiency. The high porosity, large specific surface area, and cation exchange capacity of zeolite support the growth and fixation of microorganisms. Tang *et al*. (2023a) reported that the optimal zeolite particle size (0.2–0.5 mm) resulted in methane production of up to 186.75 mL CH_4/g VSS. Similar findings were also reported by Pampang and Purnomo (2024), who found that the addition of zeolite in a fixed-bed reactor could increase sCOD removal efficiency by up to 89.66%. This indicates that the physical and chemical structure of zeolite greatly supports the formation of biologically active biofilms (Harun *et al*., 2021).

Meanwhile, bioceramics also exhibit considerable potential as a support medium in anaerobic reactors. Bertin *et al.* (2010) revealed that the use of bioceramic filters as a biofilm medium increases COD degradation and supports the formation of a stable bacterial community during the acidogenesis process. Additionally, porous media such as zeolite and bioceramics not only provide mechanical support, but also create a microenvironment conducive to the growth of methanogenic microorganisms. Therefore, the selection of media with appropriate physical characteristics, such as mechanical stability and pore distribution, was an important aspect in the design of an efficient anaerobic reactor (Paritosh *et al.*, 2020).

Understanding kinetic parameters such as maximum microbial growth rate, substrate affinity constant, and reaction rate constant is essential in designing and optimizing anaerobic reactors. Kinetic analysis provides clear insights into the biodegradation efficiency and biogas production potential of a system. Montalvo *et al.* (2012), highlights the role of zeolite as an NH_4^+ adsorbent and microbe habitat builder, which accelerates biofilm formation and biogas production. In addition, the incorporation of zeolite has been shown to shorten the lag phase and increase production efficiency. Recent studies have reported the effectiveness of each medium in enhancing biogas production (Tang *et al.*, 2023b). However, direct comparative studies of kinetic parameters between media under uniform reactor conditions are still limited, especially in the context of dairy industry waste treatment.

Therefore, this study aims to fill this gap with a systematic approach to evaluating and comparing the kinetic parameters of biogas production from the sludge waste of the dairy industry in a batch-type fixed-bed anaerobic reactor using zeolite and bioceramics as the immobilizing media. Unlike continuous stirred-tank reactors (CSTR), the fixed-bed reactor used in this study considers mass transfer resistance and diffusion limitations as a consequence of biofilm formation on the immobilizing media. Therefore, the kinetic parameters obtained represent apparent kinetics, integrating both transport phenomena and biological reaction rates. This approach better reflects practical anaerobic digestion systems employing immobilized biomass. The results of this study are expected to contribute to the development of more effective and sustainable dairy industry waste treatment technology.

MATERIAL AND METHOD

Substrate and immobilization Media

This study used liquid sludge from the dairy processing industry waste as the main substrate in the anaerobic digestion process. It was obtained from the industrial liquid waste treatment unit and filtered to remove coarse particles. Two types of immobilization media were used in the reactor, namely natural zeolite and porous bioceramic media (Pampang and Purnomo, 2024). Both immobilization media provide a high surface area and special pore characteristics that support the formation of microbial biofilms.

Experimental Design

The experiment was conducted in a 30-liter laboratory-scale batch fixed-bed reactor. A schematic diagram of the reactor system has been previously reported in our earlier work (Pampang and Purnomo, 2024). For clarity, the key features and specifications of the system are summarized in this study. The reactor was designed as a column with an inner diameter of 19 cm and a total height of 200 cm, with an effective working height of 150 cm. Samples were collected from three different positions along the reactor height, namely the lower, middle, and upper sections, to capture spatial variations within the system. The soluble chemical oxygen demand (sCOD) was analyzed according to the Standard Methods (APHA, 20th edition, Method 5220D). The methane content in the produced biogas was determined using gas chromatography (Shimadzu GC-8A). Biogas production was accumulated and measured using a simple gas meter, following the approach described by Walker *et al.* (2009) to ensure reliable quantification of gas volume. The initial biomass concentration (X_0) and initial substrate concentration (S_0) were set at 50 mg/L and 6553 mg/L, respectively.

The reactor was operated under anaerobic conditions at a predetermined mesophilic temperature without stirring during the fermentation process. Each reactor was filled with sludge and one type of immobilization medium to obtain reliable data on the two main treatments. Observations were made for 21 days, with samples taken on days 0, 3, 6, 9, 12, 15, 18, and 21. For reference, the reactor method and material composition in this study adapted the approach from (Pampang and Purnomo, 2024), which used a fixed-bed reactor and added 30% zeolite of the total reactor volume as a microbial support medium (Harun *et al.*, 2020). The reactor was hermetically lidded, and the biogas volume was measured based on the air displacement method. The concentration of organic compounds in the sludge was measured based on the Chemical Oxygen Demand (COD) and Volatile Fatty Acid (VFA) parameters. Meanwhile, the gas was measured in terms of volume and the concentration of methane gas produced. Samples were taken from each reactor at predetermined times and analyzed to obtain daily COD values. COD data was used to estimate substrate conversion efficiency during the process.

An apparent kinetic approach derived from the mass balance during substrate degradation and biogas generation was applied to further examine the experimental results. Despite the high possibility of intraparticle diffusion and external mass transfer resistance in immobilized systems, these effects were thought to be insignificant in the current experimental setup. The tiny particle size, vigorous mixing conditions, and the strong agreement between experimental results and kinetic model predictions all supported this idea. As a result, it was reasonable to characterize the observed behavior as mostly a reaction-controlled system. However, it should be highlighted that apparent kinetics, which may implicitly include small transport effects, were represented by the derived values. Substrate transport in immobilized systems might include dispersion effects, intraparticle diffusion inside porous structures, and external mass transfer from the bulk liquid to the particle surface. Deviations from intrinsic reaction kinetics may result from these transport events. These effects were not specifically included in the model equations of the current study. Rather, an apparent kinetic method was used, in which the predicted parameters reflect the combined effects of transport constraints and biological reactions. In situations when precise kinetic control cannot be strictly guaranteed, this method is frequently employed to describe actual immobilized systems.

Substrate Degradation Modelling

Monod kinetic model

The Monod model is one of the most basic kinetic models in bioprocess engineering, which relates the growth rate of microorganisms (μ) to the concentration of dissolved substrate (S). In the context of a batch system, this model can also be applied to describe the rate of substrate depletion, assuming that microbial growth was proportional to substrate consumption (Monod, 1949). This model can be expressed as:

$$\mu=\frac{\mu_{max}.S}{K_s+S} \quad (1)$$

and the form of substrate degradation in a batch system is written as:

$$\frac{dS}{dt}=-k\frac{S}{K_s+S} \quad (2)$$

where: μ= specific growth rate of microorganisms; μ_{max}= maximum growth rate (1/day); S= substrate concentration (sCOD) (mg/L); K_s= substrate saturation constant (mg/L); k= degradation rate constant (1/day). The Monod model is used in this research to estimate the substrate conversion rate based on sCOD changes, using a nonlinear regression approach to actual sCOD data (Contois, 1959).

Contois kinetic model

The Contois model is a modification of the Monod model that considers the influence of active microbial biomass (X) on substrate uptake. This model was generally applied to systems with high solid concentrations, such as food or livestock industry wastewater, because the presence of total solids can affect substrate accessibility by microbes. The Contois growth rate equation can be expressed as:

$$\mu=\mu_{max}\frac{S}{K_C X+S} \quad (3)$$

and the substrate degradation rate in a batch can be calculated using Equation (4).

$$\frac{dS}{dt}=-k\frac{S}{K_C X+S} \quad (4)$$

where: Kc = Contois saturation constant (L/mg), X = concentration of active biomass of microorganisms (mg/L)(Contois, 1959).

Moser Kinetic Model

The Moser model is an extension of the Monod model that incorporates the flexibility parameter n, allowing for a more flexible representation of the curve shape, including a sigmoidal shape when n ≠ 1. This model is useful when degradation data showed curvature that couldnot be optimally explained by the Monod or Contois models (Moser, 1957). The Moser kinetic equation for microorganism growth is represented by Equation (5):

$$\mu=\mu_{max}\frac{S}{(K_s+S)^n} \quad (5)$$

and for substrate degradation in a batch system:

$$\frac{dS}{dt}=-k\frac{S}{(K_S+S)^n} \quad (6)$$

The combination of logistic equations in the anaerobic batch growth curve system, taking into account endogenous metabolism through the decay constant (k_d), is used in this modeling (Shuler and Kargi, 2002). The differential equation for biomass is expressed by Equation (7).

$$\frac{dX}{dt}=(\mu- k_d)X \quad (7)$$

while, substrate consumption is expressed as follow:

$$\frac{dS}{dt}=-\frac{1}{Y}\mu X \quad (8)$$

The three models can be used to fit the sCOD reduction data during the batch process using software. The parameters k, Ks, Kc, and n can be evaluated using a nonlinear regression approach. The best model was determined based on the coefficient of determination (R^2), Root Mean Square Error (RMSE), and visual fit between the predicted curve and actual data.

Biogas Formation Modeling

First-order kinetic model

The first-order kinetic model is suitable to describe the rate of substrate (COD) reduction during the fermentation process. This model assumes that the rate of biogas formation was proportional to the amount of un-decomposed substrate. In addition, this model was simpler but effective in describing biogas accumulation in a batch system.

$$G(t) = G\infty\ (1-e^{-kt}) \quad (9)$$

where: G(t)= cumulative biogas volume at time t (mL); G∞= theoretical maximum biogas yield (mL); k = biogas formation rate constant (1/day); t = time (days). This model is suitable for estimating total accumulation without considering the lag phase (Hashimoto, 1986)

Modified Gompertz kinetic model

The modified Gompertz model can be applied to model the cumulative accumulation of methane gas during the digestion process. This model was widely used to model biogas production due to its ability to represent the lag phase, maximum rate, and saturation phase. The model is expressed as:

$$G(t)=A.\exp\left(-\exp\left(\frac{R_m.e}{A}(\lambda-t)+t\right)\right) \quad (10)$$

where: A= maximum potential biogas production (mL); Rm= maximum rate of biogas production (mL/day); λ= lag phase (days). This model is considered more realistic than the first-order model, especially for systems with a clear microbial adaptation phase (Noike *et al*., 1997).

Modified logistic kinetic model

The modified logistic model is an alternative to Gompertz, but assumes symmetry in the acceleration and deceleration rates of gas production. The model equation was:

$$G(t)=A\left(1+\exp\left(\frac{4R_m}{A}(\lambda-t)+2\right)\right)^{-1} \qquad (11)$$

This model is suitable for systems where the initial and final production rates are nearly symmetrical, and it provides a more conservative estimate of the lag phase(Zwietering *et al*., 1990).

Transfer kinetic model

The Transfer Model, also known as the Cone Model, was developed to account for the dynamics of delay time and the rate of substrate transfer to microorganisms. This study's kinetic models were based on a pseudo-homogeneous (apparent) approach that treated the reactor system as a single effective phase. The model equations did not specifically account for transport phenomena such as axial dispersion, intraparticle diffusion, and external mass transfer. Rather, it was presumed that the computed kinetic parameters implicitly included these effects. For practical modeling of immobilized systems, where the main goal was to characterize the overall reactor performance rather than specific transport-reaction interactions, this simplification is frequently used.

$$G(t) = G\infty(1 - e^{-kt^n}) \qquad (12)$$

Where, n is the structure exponent (cone parameter), typically $0.5 \leq n \leq 2$. This model was flexible and capable of adjusting the curve shape based on substrate type and waste structure complexity. This model was particularly useful for high-solids systems or slow-degrading substrates (Pitt *et al*., 1999). All four models were used to fit cumulative biogas volume data during fermentation. The lumped parameter approach, which describes cumulative biogas production as a function of time, was the foundation of the kinetic models used in this investigation. Methane generation and substrate concentration (sCOD) spatial changes along the reactor height were not specifically taken into account. The creation of governing equations that take into account mass balances, transport phenomena, and reaction kinetics in a distributed system would be necessary for a more rigorous modeling framework. Such complexity, however, was outside the purview of this work and was suggested for further research. Parameter estimation was performed through nonlinear regression using MATLAB R2024a, and the models fit were evaluated using R^2, RMSE, and other parameters, as well as visual verification against experimental data.

RESULTS AND DISCUSSION

Evaluation of Empirical Models for sCOD Reduction

The kinetics of milk sludge waste (MSW) substrate decomposition using a reactor filled with zeolite media was indicated by a decrease in sCOD concentration from the first to 21st days, with an initial sCOD concentration of 6553.59 mg/L. Each treatment was performed in duplicate to ensure data reliability (Harun *et al.*, 2020). Degradation was modeled using three types of approaches, ie, the Monod, Contois, and Moser models. Table 1 presents the Constants of Monod, Contois and Moser models for zeolite and bioceramic. The fitting results in Figure 1 show that the Moser model provided the best fit for the substrate degradation data (μ_{max}) with a decrease in sCOD concentration in the reactor filled with zeolite media, where the degradation rate was 0.0178 h^{-1} with an R^2 of 0.9287 and an RMSE value of 500.12 mg/L, then followed by the Monod model with a degradation rate of 0.9×10^{-3} h^{-1} with an R^2 of 0.8950 and an RMSE value of 606.78 mg/L, while the Contois model showed a lower fit with an R^2 of 0.8325 and an RMSE value of 766.27 mg/L. The application of the Moser model to zeolite media produced an exponential constant (n) value of 2.9179, which is significantly higher than the Monod model assumption. The n value greater than one indicates the presence of positive synergy in biological systems, where the microbial growth rate becomes more sensitive to changes in substrate concentration (Moser, 1988). Physically, the superior performance of this model was supported by the characteristics of zeolite, which has a high specific surface area and a pore structure that can protect the biofilm from organic load fluctuations (Wang and Peng, 2010; Montalvo *et al.*, 2012). These findings were consistent with previous studies showing that the Moser model can better describe substrate degradation efficiency at low COD concentrations than the Monod model (Owhondah *et al.*, 2016; Muloiwa *et al.*, 2020). In general, these results indicate that the Moser model was more capable of capturing the dynamics of substrate degradation in reactors using zeolite media. This phenomenon was consistent with previous studies emphasizing the role of porous media such as zeolite in enhancing biofilm colonization, maintaining local substrate concentration, and reducing the inhibitory effect of ammonia (Pirsaheb *et al.* , 2019; Tang *et al.*, 2023a). Zeolite was also capable of enhancing a stable microenvironment by maintaining pH, thereby ensuring a more consistent substrate degradation process.

The results of substrate decomposition fitting using the reactor filled with bioceramic media are shown in Figure 2. All models show better fit than zeolite. The Monod and Moser models ranked highest with an R^2 of 0.9939 and RMSE values of 111.73 mg/L and 112.17 mg/L, respectively. Then followed by the Contois model with an R^2 of 0.99684 and an RMSE value of 254.74 mg/L. The n value in the Moser model with a bioceramic reactor filling of 1.54 indicates that substrate degradation occurs with a more homogeneous tendency after the initial adaptation phase, which is consistent with the properties of bioceramics as a relatively stable inert material (Bertin *et al.*, 2010). The Moser model excels in representing substrate degradation in both media, showing that the consumption pattern did not fully follow the classic Monod form. The results show a significant difference between the use of zeolite and bioceramic media in anaerobic fixed bed reactors. In zeolite media, the Moser model provides the best fit with an exponent (n) value closer to one, indicating that substrate degradation remains effective even at low substrate concentrations and with a short adaptation phase followed by accelerated degradation, but its characteristics are still close to Monod.

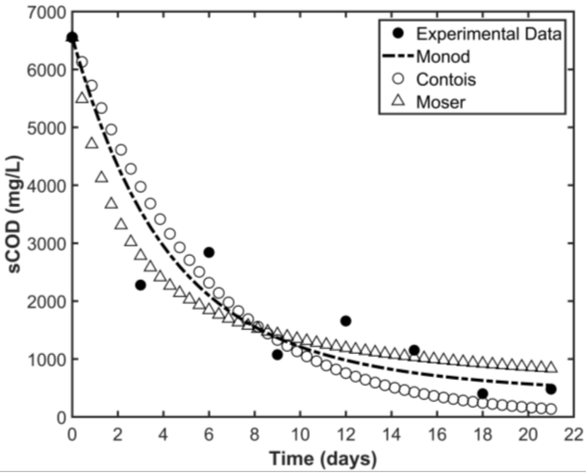

Figure 1. Kinetic model for substrate degradation using zeolite media

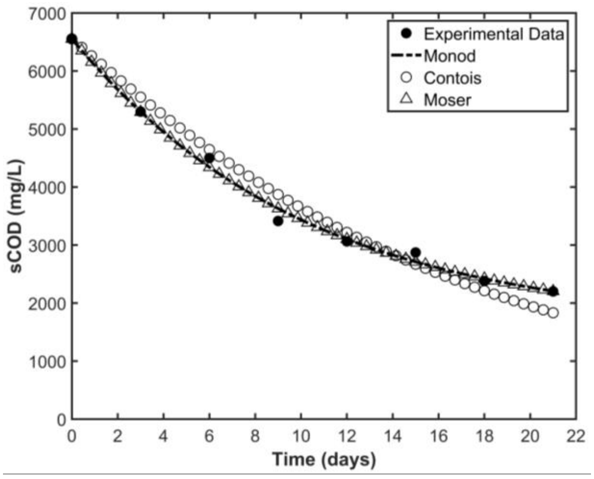

Figure 2. Kinetic model for substrate degradation using bioceramic media

This was consistent with the role of zeolite as a porous medium with high cation exchange capacity, which was able to absorb ammonium ions and reduce toxicity to methanogens. The phenomenon of increased process stability and biofilm formation in zeolite systems has also been reported, where zeolite was able to improve microbial colonization, reduce inhibitory effects such as ammonia and long-chain fatty acids (LCFA), and stabilize anaerobic digestion performance (Tang *et al.*, 2023b; Wang *et al.*, 2024). Conversely, in bioceramic media, all models showed better performance. Values significantly less than one in bioceramics indicate a more homogeneous and rapid degradation pattern after the adaptation phase, where the degradation rate remains relatively constant without significant acceleration. This can be attributed to the more chemically inert nature of bioceramics, which provide a large surface area for biofilm and more even substrate distribution, so that although they were able to retain biofilm, they did not have an adsorptive effect on inhibitory ions. As a result, substrate degradation was more stable but did not reach the high rates seen with zeolites.

Recent studies also reported that bioceramic-type media often produce more uniform microenvironmental conditions, making kinetic models more precise. On the other hand, bioceramics are generally used to enhance process stability due to their large pores and durable mechanical properties (Zamrisham *et al.*, 2024). These mechanistic differences explain why kinetic parameter values in bioceramics appear more stable, but gas production was relatively low. Thus, although zeolite provides specific benefits in terms of mitigation of inhibition and support for local biofilms, bioceramics appear to be superior in producing consistent sCOD degradation patterns with higher model fit. This was in line with recent studies emphasizing that media selection has a direct impact on kinetic parameters, including the Moser exponent (n) (Wu *et al.*, 2024).

In addition to sCOD degradation parameters, the methane formation profile provides a more comprehensive picture of the effectiveness of the microenvironment in the reactor. Based on the observations in Figure 3, the zeolite media showed significant superiority, with methane concentrations peaking at 37.82% on day 6, far exceeding bioceramic medium, which remained below 10% throughout the operational period. This was in line with a significant decrease in sCOD to 480.07 mg/L, while the bioceramic medium was only able to reduce it to 2201.15 mg/L. The low methane production in the bioceramic medium, despite its good substrate decomposition kinetic stability with R^2 of 0.9939, indicates the occurrence of acidosis, where organic degradation stops at the acidogenesis phase without continuing to the effective methanogenesis stage. This phenomenon can be explained by the cation exchange capacity (CEC) possessed by zeolite but not by inert bioceramics.

Table 1. Constants of Monod, Contois and Moser models for zeolite and bioceramic

Media	Parameter	Monod	Contois	Moser
Zeolite	μ_{max} (1/day)	0.9×10^{-3}	2	0.0178
	Y (mg VSS/mg sCOD)	1.259×10^{-5}	0.2078	2.048×10^{-5}
	k_d (1/day)	0.1	0.1	0
	Ks (mg/L) / Kc (L/mg VSS)	1×10^4	50	1×10^4
	X	-	500	-
	n	-	-	2.9179
	R^2	0.8950	0.8325	0.9287
	RMSE (mg/L)	606.78	766.27	500.12
Bioceramic	μ_{max} (1/day)	0.1536	2	0.6050
	Y (mg VSS/mg sCOD)	0.0064	0.6148	0.2×10^{-3}
	k_d (1/day)	0.1	0.1	0.0808
	Ks (mg/L) / Kc (L/mg VSS)	9999.78	50	5204.41
	X	-	500	-
	n	-	-	1.5386
	R^2	0.9939	0.9684	0.9939
	RMSE (mg/L)	111.73	254.74	112.17

Zeolite acts as a mitigating agent against ammonia inhibition, which often occurs in the treatment of high protein waste such as milk sludge.

Zeolite's ability to absorb ammonium ions (NH_4^+) creates stable micro-pH conditions for the methanogenic bacteria to multiply (Montalvo *et al.*, 2012; Wang *et al.*, 2024). This was in line with the Moser exponent (n) value in zeolite, which reaches 2.9179, reflecting the acceleration of microbial growth that was more responsive to substrate availability compared to bioceramics. Therefore, the use of zeolite not only optimizes the kinetic efficiency of organic material degradation but also functionally improves energy recovery quality in the form of higher methane purity compared to other support media (Poirier *et al.*, 2017).

Biogas Production Kinetics and Performance Evaluation

The kinetics of biogas formation using a fixed bed anaerobic reactor were modeled using several approaches, namely First Order, Gompertz, Logistic, and Transfer (Cone) as shown in Figure 3. From the results of modeling the cumulative biogas production curve in a reactor containing zeolite, it was best represented by sigmoid models, especially the Cone Model with an R^2 value of 0.9970 and an RMSE value of 354.8744 mg/L. The Transfer model showed the best performance among all parameter models with a biogas potential of 17.1372 L and a rate constant k of 0.1498 d^{-1} and a factor n of 3.167. The n value greater than one indicates a more sigmoidal curve shape, thus better capturing the lag and acceleration phases of production. These results confirmed that the Cone model was superior in describing the dynamics of biogas production from complex substrates, although its use was not yet as popular as Gompertz. The Gompertz parameters indicate a maximum biogas potential A of 16.5845 L with a maximum rate R_m of 2.1689 L·d^{-1} and a lag time (λ) of 2.75 d. These values were consistent with biological conditions, where the adaptation phase was relatively short before biogas production increased sharply. The modified Gompertz model has an R^2 value of 0.9957 and an RMSE value of 423.1504 mg/L, indicating the ability of the Gompertz model to represent the sigmoidal growth curve of substrate degradation. This finding was in line with previous studies reporting that the modified Gompertz was often the most representative model for cumulative biogas production, whether in food waste, manure, or lignocellulosic biomass (Mohammadianroshanfekr *et al.*, 2024). Both were able to capture the lag phase, acceleration, and saturation point. The high A value indicates the high methanogenic potential of dairy industrial sludge waste substrate when processed with zeolite as an immobilization medium. The R_m value was relatively high compared to similar batch sludge studies, where the average peak rate was in the range of 500 – 1,500 mL.d^{-1} (Wang *et al.*, 2024). The Logistic model produced estimates comparable to Gompertz, with a biogas potential of 16.1615 L with an R_m value of 2.279 L/.d^{-1} and a lag time (λ) of 3.12 d. However, the higher RMSE value of 603.9172 mg/L compared to Gompertz indicates a greater deviation, especially in the early and late stages of degradation. This was in line with the relatively symmetrical characteristics of the Logistic model, which was less flexible in describing the actual asymmetry in biogas production patterns

(Pramanik *et al.*, 2019). This indicates that zeolite significantly accelerates the conversion of substrate into methane. The short lag phase shows that the biofilm quickly adapts to the zeolite surface. This condition can be explained by the microporous structure of zeolite, which provides niches for acidogenic and methanogenic bacteria, as well as the ionic buffer effect that maintains micro-pH stability. These results were in line with the findings of Poirier S. et al., who reported that the use of zeolite reduced the lag phase of biogas production by 47% compared to the control without immobilization media (Poirier *et al.*, 2017). This value was higher than the logistic model with a lag time, biogas production, and the rate described above, although the difference was relatively small. Gompertz emphasizes the importance of using a sigmoidal model. The first-order model produced a biogas potential value of 23,3425 L with a rate constant of k at 0.0699 d^{-1}. Although it provides a simple description, this model showed the lowest fit with the experimental data, as seen from the R^2 value of 0.9482 with an RMSE of 1467.6793 mg/L. This indicates that the first-order model tends to overestimate biogas production potential because it can not capture biological phenomena such as the lag phase and maximum production rate limitations. Thus, this model was more suitable for use as an initial approach for simple substrates but was less representative for complex systems (Olatunji *et al.*, 2025). The high R_m and relatively short λ indicate that zeolite media can accelerate the start-up phase of methanogenesis and maintain the growth rate of methanogens. This was most likely due to two mechanisms, ie, biomass retention on the porous zeolite surface, so that methanogens remain bound despite substrate fluctuations, and the ability of zeolite to absorb free ammonia (NH_4^+), thereby reducing the risk of inhibition often encountered in anaerobic decomposition processes (Tang *et al.*, 2023b; Wang *et al.*, 2024).

The biogas production curve on bioceramic media in Figure 4 showed much lower results compared to zeolite, with model parameters that were difficult to interpret. Fitting with Gompertz and Logistic produces A values of only about 129.5860 mL and 127.0148 mL with rates R_m of about 9.5818 mL·d^{-1} and 8.6826 mL·d^{-1}, but both have negative λ, indicating parameter identification problems or data that did not support lag phase estimation well. This was most likely due to low gas production, causing the kinetic parameters to be lost in measurement variations. The Cone model gave different results with A of 6,09 L, while the first-order model also showed a low A of 132.9716 mL, which was inversely proportional to the biogas production in the zeolite medium. This showed that the bioceramic medium did not support gas accumulation under these experimental conditions, even though the bioceramic substrate degradation stage showed better stability than zeolite.

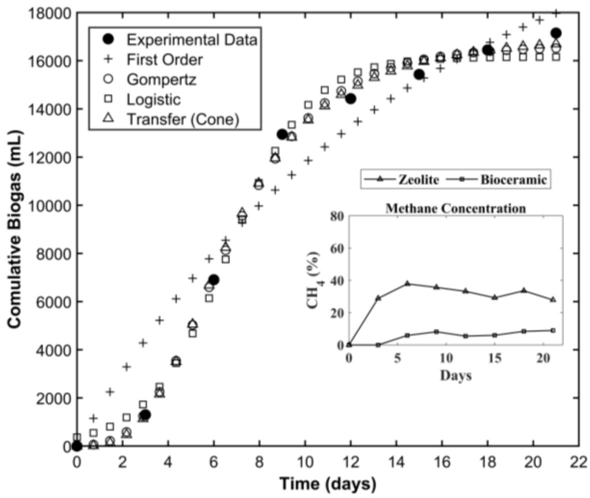

Figure 3. Biogas formation model fitting graph of zeolite media

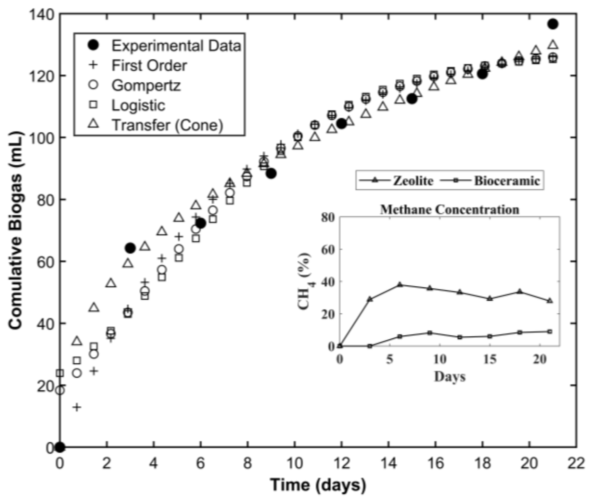

Figure 4. Biogas formation model fitting graph of bioceramic media

This phenomenon also emphasizes that although bioceramics had large pores that support biofilm, there were no additional mechanisms such as the absorption of inhibitory ions. As a result, methanogens may grow more slowly or experience stress due to ammonia accumulation. The use of bioceramic media tends to produce long-term stability, but the increase in biogas production was relatively limited. Syguła *et al.* (2023) reported that the addition of porous ceramic powder only modified methane yield within a maximum range of 4.6% compared to the control, meaning that it only slightly increased methane production. The use of bioceramic media tends to produce long-term stability, but the increase in biogas production was relatively limited. Meanwhile, Zamrisham *et al.* (2024) found that to increase methane production, it was necessary to integrate ceramic bio-rings with red clay and lava rock in the reactor. These findings confirm that the single use of bioceramic media in anaerobic processes was less effective in producing methane and also less effective in accelerating the start-up phase compared to active media such as zeolite. From a practical perspective, bioceramics may be more suitable for continuous applications with longer hydraulic retention time (HRT), where the advantages of medium stability are more relevant than accelerating initial gas production. In general, these results confirm that the First Order and Cone models were most suitable for predicting biogas production, as they were able to accommodate the lag phase, maximum production rate, and asymmetry in the degradation curve. The Logistic and Gompertz model remained relevant as a comparison, while the first-order model was only suitable as a simple baseline. Thus, selecting the appropriate model was not only important for improving prediction accuracy but also for understanding the biological mechanisms underlying the anaerobic digestion process. The correlation between substrate consumption rate and methane production rate showed a direct relationship in zeolite media. Higher μ_{max} values from the Moser or Monod models correlate with larger R_m Gompertz values, confirming that substrate degradation was the main driver of gas production. The scatter plot between daily sCOD consumption and R_m showed a positive trend where $R^2 > 0,9$. In comparison, zeolite showed much greater potential for biogas production and R_m than bioceramics. Conversely, in bioceramics, this relationship was not clearly seen due to low gas production and parameter identification issues. These findings were consistent with the report by Montalvo S., which emphasizes that the efficiency of substrate conversion to methane was greatly influenced by the properties of the immobilization medium (Montalvo *et al.*, 2012).

In terms of substrate degradation, bioceramics showed degradation stability using the Moser model with an R^2 of 0,9939 but were unable to translate this into significant methane accumulation. Conversely, zeolite, despite its more fluctuating degradation, showed superior performance in the methanogenesis stage. This was in line with reports from several studies that also obtained high methane production using zeolite media (Tang *et al.*, 2023b; Wang *et al.*, 2024). The practical implication of these results was that zeolite was more suitable for batch systems that require accelerated start-up and high gas production. Bioceramics can be considered in continuous systems with longer residence times, where substrate degradation stability is prioritized. However, to improve the performance of bioceramics, further engineering of size, porosity, and pore distribution was needed to better support biomass retention and substrate diffusion. It is important to note that although the kinetic model used in this study showed a high statistical correlation, there were inherent limitations in interpreting the results biologically. First, conventional microbial growth kinetic models often fail to specifically distinguish between sCOD degradation that was truly converted to methane and decomposition that produces other byproducts such as CO_2, H_2S, or ammonia accumulation due to the high nitrogen content in milk sludge (Wang *et al.*, 2024). This leads to the risk of misinterpretation where the model appears to fit mathematically but does not reflect the actual energy conversion efficiency. Second, the phenomenon observed in Figure 4 showed that model stability was not always directly proportional to methane productivity. Bioceramic media, despite producing excellent modeling data, actually produced much lower methane volumes and concentrations than zeolite. The model's inability to capture these variations in gas composition was due to its nature of simplifying multicellular biochemical reactions into a single parameter, thereby failing to follow the dominant gas distribution patterns formed in heterogeneous systems (Ruiz-Bastidas *et al.*, 2024). The multitude of micro environmental factors and the diversity of acidogenesis to methanogenesis reactions limit deterministic models in accurately predicting gas quality fluctuations, especially in media that lack mitigation inhibition capabilities such as bioceramics (Rongrong *et al.*, 2024).

CONCLUSION

This study showed that the selection of filling media played an important role in determining the kinetic characteristics of substrate decomposition and biogas formation in the anaerobic digestion of dairy industry waste. The Moser model proved to be the most suitable for describing sCOD degradation in both types of media, with the highest R^2 value compared to the Monod and Contois models. The exponent n value in zeolite, which was close to one, indicates high substrate degradation efficiency under low substrate conditions, while bioceramics show more stable and homogeneous degradation without additional adsorptive effects. In terms of biogas formation, the Transfer (Cone) and Modified Gompertz models provided the best fit for the experimental data with R^2 above 0.99. Zeolite media produced a maximum biogas potential of 17.14 L with a maximum rate of 2.17 $L \cdot d^{-1}$, kinetic constant (k) of 0,1498 d^{-1}, and a lag phase of 2.75 days, indicating rapid microbial adaptation and high methanogenesis efficiency. In contrast, bioceramics produced lower gas volumes and unstable formation rates, indicating limited mass transfer and low methanogenic microbial activity in this medium. The positive correlation between the μ_{max} and R_m parameters confirmed that an increase in the substrate degradation rate was directly proportional to methane production efficiency. Overall, zeolite was more suitable for batch systems that require accelerated start-up and high gas production, while bioceramic had more potential for continuous systems that require long-term process stability. The development of active porous media or hybrids between bioceramics and absorbent materials such as zeolite is recommended to improve kinetic performance and biogas conversion efficiency in the future.

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