

Kinetic Modeling of Methane Production from the Anaerobic Digestion of Wastewater Sludge from a Treatment Plant in Kenitra, Morocco

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ABSTRACT

It is necessary to understand the process of anaerobic digestion (AD) of sewage sludge and to find an adequate strategy to improve the efficiency of methane production. In this work, the production of methane and detailed properties of sludge are determined. The physico-chemical parameters of the digester 1 'D1' and the digester 2 'D2' remain in the optimal range of AD stability with a median value of pH (7.82; 7.93); Temperature (36.70; 37.10°C); alkalinity (3.52; 3.58 g/L); and volatile fatty acids (0.47; 0.52 g/L), respectively. This paper focuses on the performance optimization of the methane production by kinetic models of two continuous digesters in a wastewater treatment plant in Kenitra City, Morocco. Mathematical models used in anaerobic digestion are: Modified Gompertz, transference functions, and logistics functions. These kinetic models have benefitted experimental methane production for both digesters. Results show that all the models used are appropriate to optimize the kinetic parameters for producing methane, showing that the transference function is the most suitable model for predicting kinetic results.

Keywords: wastewater treatment plant, anaerobic digestion, sewage sludge, methane production, kinetics modeling.

INTRODUCTION

Rapid economic development in all sectors, including industry, agriculture and transport, has led to an increase in energy demand, resulting in an energy crisis (Usmani et al., 2021) a sugar-ethanol residue, is used as a substrate for biogas production. The characteristics of the vinasse wastewater used were 216,000 mg-COD/L, pH 4.1, and 68.42 mg/L volatile solids. The sludge/wastewater ratio was controlled at about 1.5–2.0, by weight. Biogas production enhancement was studied in relation to two parameters – Citadel BioCat p , a commercial biocatalyst containing a large microorganism population as the methanogenic bacteria source (5 and 10 g, reflected in the depletion of fossil fuel reserves and environmental degradation. Therefore, it is essential to

emphasize the sustainable economic use of existing limited resources. But also to identify new technologies that are capable of meeting the growing demand for energy. (Prajapati et al., 2018). In recent years, wastewater treatment plants have fully participated in the emergence of a territorial circular economy where our wastewater becomes an agronomic and energy resource thanks to the methanization process (Dai et al., 2016). Anaerobic digestion (AD) is a biological process that degrades organic matter of waste into a valuable product (Bakraoui et al., 2020; Lahboubi et al., 2020). AD produces two main products: biogas and digestate. The biogas composed mostly of methane and carbon dioxide

(Bakraoui et al., 2020; Karouach et al., 2020). AD is considered as the most energy efficient and environmentally friendly method of sludge

degradation (Donoso-Bravo et al., 2011), and is the ideal solution for wastewater treatment plants (Makisha et al., 2018). This process has the advantage of not only stabilizing the sludge by reducing its organic content, but also producing methane that can be used for renewable energy (Mohd et al., 2015) specifically at 45°C. Single-stage batch anaerobic digestion system was developed in the lab and performance was monitored for more than 2 years. The AD system was able to achieve high biogas production with about 62% - 67% methane content. The digester exhibited high acetate accumulation, but sufficient buffering capacity was observed as the pH, alkalinity and volatile fatty acids-to-alkalinity ratio were within recommended values. The system achieved 36.5% reduction of total solids (TS).

In Morocco, the city of Kenitra has a wastewater treatment plant installed to treat pollution with a capacity equivalent to 334.000 inhabitant equivalents. It can treat up to 53.900 m³ of wastewater per day with an average flow rate of 2.250 m³/hour and a production of 6.700 Nm³ of biogas per day. The produced biogas contains about 70% methane. The biogas is purified into methane and recovered either in a boiler or by cogeneration – caloric electricity. The produced methane covers more than 50% of the energy required by the station. The fluctuating production of methane highlights the digestion process and leads to questions about its physico-chemical parameters. This process is considered the heart of the sludge line and allows both the degradation of organic matter and the realization of self-production rate energy that the plant needs. The physico-chemical parameters have a direct impact on its success and efficiency (Tyagi et al., 2009). This highlights the importance of monitoring its parameters and improving its performance. To date, previous studies have mainly focused on analyzing the degradation of organic wastes, including wastewater and sludge, and improving degradation efficiency through various pre-treatment methods, mono-digestion, and co-digestion through anaerobic digestion (Li et al., 2017). This method is useful for understanding the process of transformation and degradation of organic matter controlled by microorganisms when examining the reaction rate, mass transfer properties, and the impact on internal dynamics in different stages of the AD process (Li et al., 2015; Ma et al., 2015). Several kinetic models analyze organic matter degradation and methanogenic production, in order to validate the most appropriate model to

the experimental results (Habchi et al., 2022). The kinetics of hydrolysis have often been modeled according to the first order kinetics model (Li et al., 2017). The kinetic modeling allows determining the maximum production rate and lag phase for methane production using different kinetic models. The modified Gompertz was used to evaluate the anaerobic digestion parameters based on methane production results (Naran et al., 2016). The logistic modeling assumes that the biogas production rate is directly proportional to the volume of gas already formed, the maximum production efficiency, and the optimal biogas production possibility (Gandhi et al., 2018). Transference function is an adequate model to use for the easily biodegradable substrate and also for negligible lag phase in biogas production (Panigrahi et al., 2020).

The aim of this paper is to evaluate the methane production under mesophilic conditions for two continuous anaerobic digester, which run in the same conditions. To this end, the physico-chemical characteristics of the sewage sludge from the two digesters were monitored continuously during the months of May and June, 2021. In addition, the kinetic modeling is evaluated by statistical models to determine kinetic parameters. The kinetic models used in this study are: Modified Gompertz, Logistic and Transference Functions.

MATERIALS AND METHODS

Reactor design

The wastewater treatment plant is composed of two identical anaerobic digesters. The reactors are working under mesophilic conditions at 37°C by the boilers. The mixture is obtained by “bubbling” the biogas in the digester. The dimensions of the digesters are shown in Table 1.

Substrate characteristics

The substrate used in this study was the sludge of Wastewater Treatment Plant in Kenitra City, Morocco; collected from the various treatments which was anaerobically stabilized. The thickened primary and secondary sludge is transferred and stored in the undigested sludge tank. This tank also receives oil and grease from the pre-treatment scum and floats from the clarification; then pumped to the anaerobic sludge digesters. The characteristics of Sludge are presented in Table 2: total solids (TS),

Table 1. Dimensions of the digesters

Dimensions of the digesters		
Units	Digester 1 'D1'	Digester 2 'D2'
Volume of the cylindrical part	4,357 m ³	4,357 m ³
Useful cylindrical height	12 m	12 m
Diameter	21.5 m	21.5 m
Total volume per unit	4,613 m ³	4,613 m ³
Total volume	9,226 m	

Table 2. The average values of all physico-chemical sludge parameters for the two digesters

Parameters	Unit	Average values digester 1	Average values digester 2
Total solids	(g/L)	41.48	46.45
Volatile solids	(g/L)	30.25	33.17
Volatile fatty acid	(g/L)	0.70	0.68
Alkalinity	(g/L)	4.29	4.31
Temperature	°C	36.46	36.27
pH	-	7.85	7.82

volatile solids (VS); volatile fatty acid (VFA); alkalinity; temperature. According to the table, both digesters run in good conditions for anaerobic digestion processes (Bakraoui et al., 2020).

CHEMICAL ANALYSIS

Measurement of total solid and volatile solid

Total solid: The samples are placed in aluminum cups. These cups were weighed empty to obtain the weight P1. 50 ml of sample is placed in each cup. The cups are then placed in an oven at 105°C for 24 hours. The next day the samples are placed in the desiccators for half an hour. They are then weighed and the weight P2 is obtained. The following formula is used to calculate the total solid (TS) value in g/L:

$$TS = ((P2 - P1) \cdot 1000) / V \text{ sample} \quad (1)$$

Volatile solids: After weighing, the samples are placed in a muffle furnace at 550°C for two hours. The weight P3 is obtained. The VS value is expressed in g/l, and is obtained by the following formula:

$$VS = ((P2 - P3) \cdot 1000) / V \text{ sample} \quad (2)$$

Measurement of alkalinity and volatile fatty acid (VFA)

The extraction of the liquid phase of the sludge consists in carrying out washes, using a 50

ml graduated cylinder previously rinsed with the sludge sample to be analyzed, 25 ml of the sample was taken and then centrifuged at 5000 t/min for 10 minutes to eliminate the supernatant and the residual pellet was resuspended in distilled water until 50 ml, rinsing with 50 ml was carried out three times.

Measurement of alkalinity

Alkalinity is obtained by titrating the solution obtained after the extraction phase described above with an acid until pH reached the value of 4. The general formula for determining alkalinity is as follows:

$$\text{Alkalinity} = V \cdot 0.2 \quad (3)$$

Measurement of volatile fatty acid (VFA)

On the same sample as the alkalinity; acid was added to bring the pH to 3.5 and the sample is boiled for 3 minutes and then cooled to room temperature. The pH is adjusted to 4 by adding a volume (A) of soda, then a titration is made until a pH of 7 is reached and V (B) is the volume obtained. The general formula for determining volatile fatty acid is as follows

$$\text{Volatile fatty acid (VFA)} = V (B) \cdot 0.24 \quad (4)$$

Biogas measurement

The biogas volume is measured every hour by a flow meter.

Biogas cleaning

The biogas produced may contains significant amounts of pollutants including H₂S. The gas is scrubbed biologically on a scrubber. This solution allows the H₂S content to be reduced without producing a polluting ultimate byproduct.

Biogas storage and excess biogas disposal

Biogas that is not used by the cogeneration process is directed either to the gas meters or to the flares (Figure 1).

Kinetic study

In this study, the logistic function, the modified Gompertz and transference function models were applied to evaluate methane production and the kinetic parameters for each model used. These models fitted the experimental results to determine the maximum production rate and lag

phase. Table 3 shows the different equations of kinetic models used.

RESULTS AND DISCUSSION

Evolution of pH

The results of the pH are shown in Fig. 2 of digester 1 ‘D1’ and digester 2 ‘D2’ for the two months of May and June, 2021. For the month of May, the pH of digester 1 varies between 7.14 and 8.56, with an overall median mean of 7.82 and for digester 2 the pH varies between 7.70 and 8.57, with an overall median mean of 7.93. The beginning of the month of May, in which we find a disturbance translated by an abrupt increase. This is justified; either by the addition of the soda which was in excess, or by the reactions of hydrolysis which were not carried out in a normal way; then one of these problems will not have the formation of the acids, which increases the pH of the

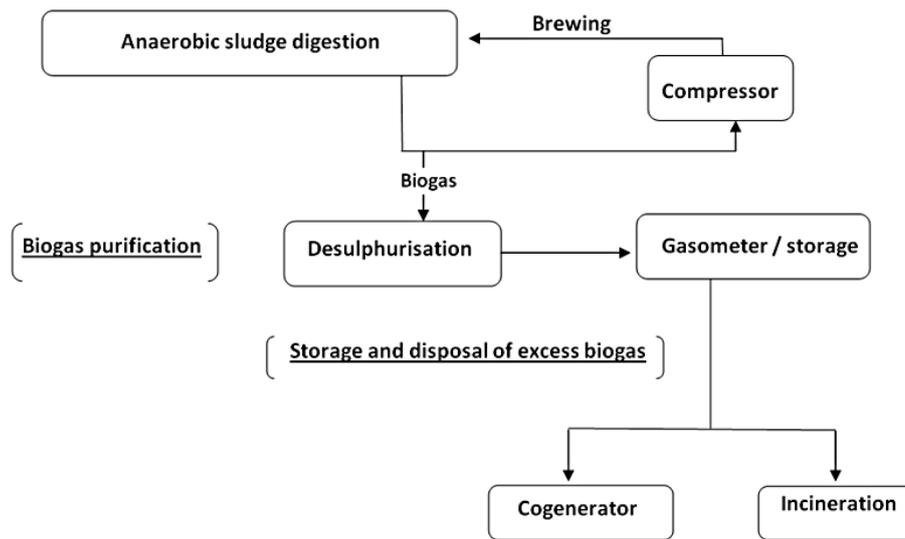


Figure 1. Diagram of biogas valorization process produced by anaerobic sludge digestion

Table 3. The different kinetic models used in this study

Model	Equation	References
Logistic function	$P(t) = \frac{A}{1 + \exp\left(\frac{4\mu}{A}(\lambda - t) + 2\right)}$	(Bakraoui et al., 2019)
Transference function	$P(t) = A * \left[1 - \exp\left(\frac{\mu * (\lambda - t)}{A}\right)\right]$	(Blasius et al., 2020)
Modified Gompertz	$P(t) = A * \exp(-\exp\left(\frac{\mu * e}{A}(\lambda - t) + 1\right))$	(Altaş, 2009)

Note: P (t) is the cumulative biogas production (m³), A is the simulated maximum biogas production (m³), μ is the maximum rate of biogas production (m³/d), λ is the lag phase (d) and t is the time of the digestion (d).

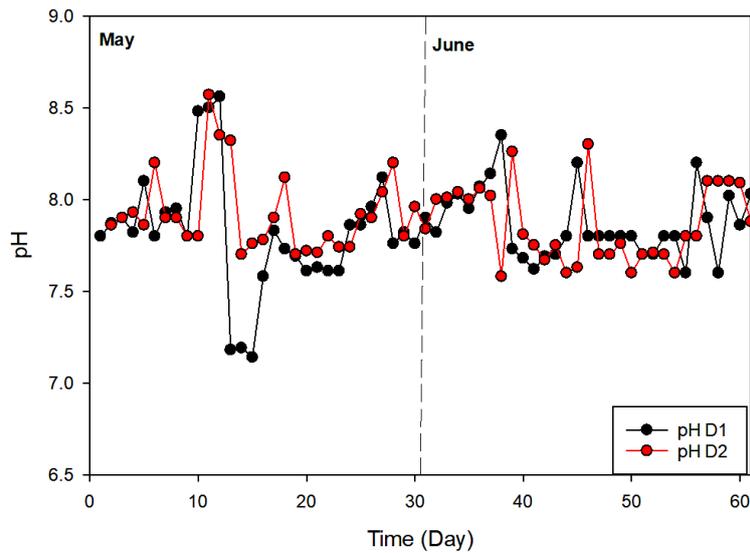


Figure 2. Evolution of pH for both digesters in May and June, 2021

digester. For the month of June, the pH of digester 1 is between 7.60 and 8.35, with an overall median mean of 7.87; and for digester 2 the pH varies between 7.58 and 8.00, with an overall median mean of 7.85. These results show that both digesters are in the optimal range of AD stability, which varies between 6.5 and 8.5 near neutrality. These results are confirmed by those of (Mtshali et al., 2014); the pH values of the sludge samples analyzed are in the desired range (between 6 and 7).

Evolution of temperature

Figure 3 shows the evolution of temperature of digester 1 and 2 for the two months of May

and June. The temperature of digester 1 for both months varies between 36.20 °C and 37.20°C, with an overall median average of 36.70 °C and for digester 2 the temperature varies between 36.10°C and 37.10°C, with an overall median average of 36.50°C. These results, which presents one of the optimal conditions of fermentation for a mesophilic digester.

Evolution of alkalinity

According to the Figure 4, the Alkalinity of digester 1 for both months varies between 3.00 and 3.84 g/L, with an overall median average of 3.52 g/L and for digester 2 the Alkalinity varies

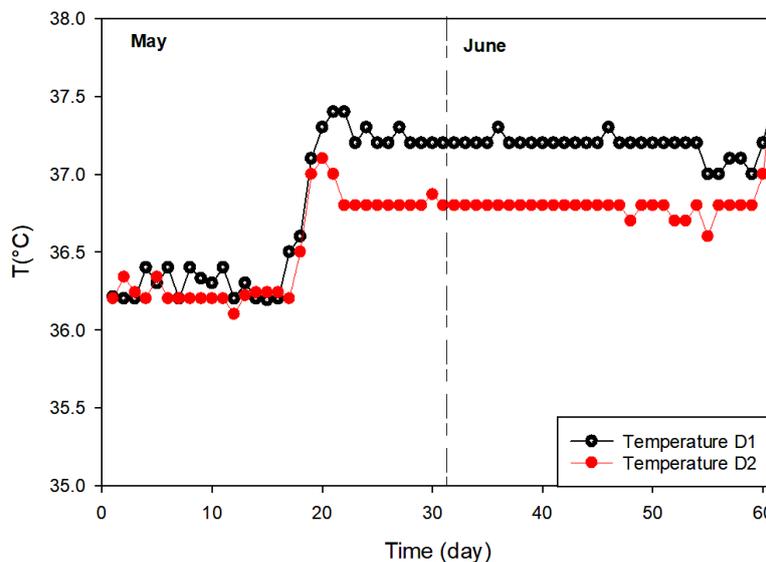


Figure 3. Evolution of temperature for both digesters in May and June, 2021

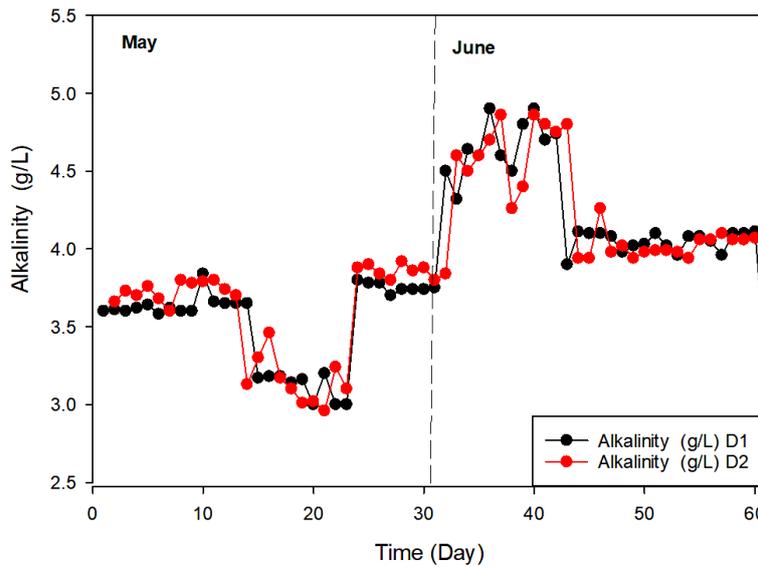


Figure 4. Evolution of alkalinity for both digesters in May and June, 2021

between 2.96 and 3.80 g/L, with an overall median average of 3.58 g/L; the Alkalinity values recorded for both digesters were above 2 g/L, so the buffer capacity of the digester is sufficient to maintain a constant pH. The buffer capacity of the digester became stable, for an operation without significant variation of the pH, more precisely without acidification of the medium.

There are several exceedances of the 0.5g/l value for each digester, which means that the methanogenesis step is not done in a normal way. VFA is therefore the ideal parameter to detect a possible overload of the system.

Evolution of volatile fatty acid

Figure 5 shows the evolution of volatile fatty acids in the two digesters. For the first digester, the value varies between 0.24 and 0.74 g/L, with an overall average of 0.47 g/L; and for the second digester, the alkalinity varies between 0.26 and 0.84 g/L, with an overall average of 0.52 g/L.

Daily methane production for two digesters for May and June

Figure 6 presents the methane production as a function of time for two digesters for May and June. We notice that the best production is visualized for the month of June with a production between 1800 and 2500 m³/day, which means that the production is better in full summer where the temperature valorizes better the production of methane for the two digesters (Fig. 6). According

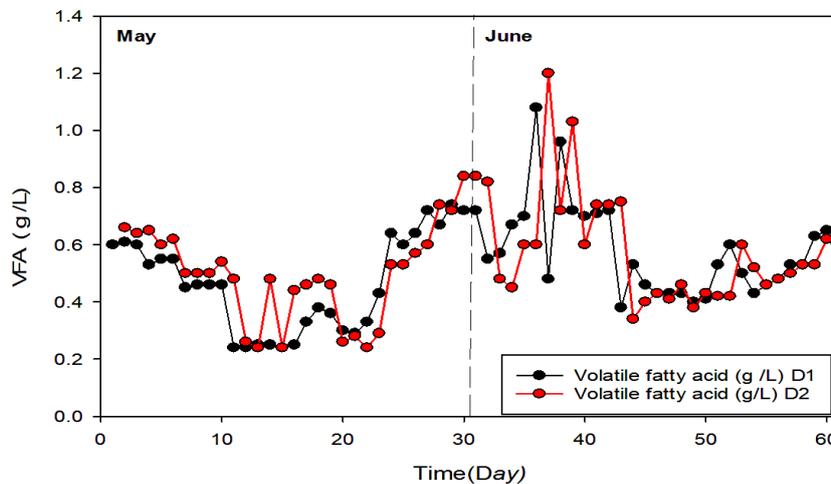


Figure 5. Evolution of volatile fatty acid for both digesters in May and June, 2021

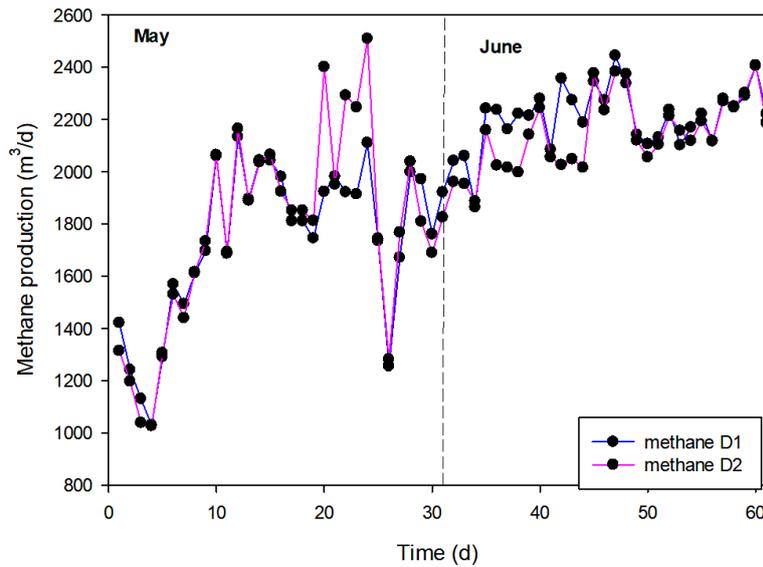


Figure 6. Methane production as function of time for two digesters for May and June, 2021

to a study of a large-scale wastewater treatment plant (WWTP) combined with batch experiments, the digester sludge’s maximal acetoclastic methanogenic activity was 70 LCH₄/kgVS·d using batch mode (Insel et al., 2022) plant-specific characterization; chemical oxygen demand (COD).

Comparative kinetic study of two continuous digesters

The kinetic parameters are important to evaluate the performance of each kinetic model used for our study; the methanogenic potential (A) (m³), the maximum rate of methane production (μ) (m³/d)

and the lag phase (λ) (d) are the principal parameters predicted. Table 4 summarizes the kinetic parameters predicted for each kinetic model. The Figure 7 present the kinetic results of two digesters for May as a function of time compared with the experimental cumulative methane production. We notice that the most adequate kinetic models and the closest to the experiment are the M Gompertz model and the transference function. For the kinetic parameters, the best lag phase is visualized at 0.45 h for the transference function equivalent to the coefficient R² of 0.9997 (Table 4).

Figure 8 represents the cumulative methane production for digester 1 and 2 for June compared

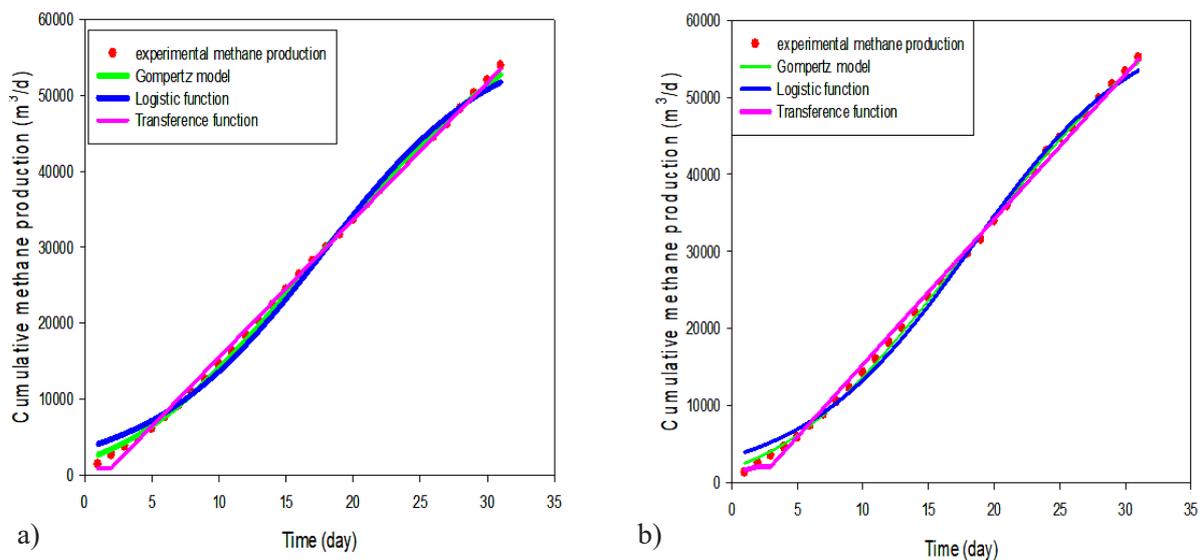


Fig. 7. Cumulative methane production and kinetic models curves as function of time for May (a) D1 (b), D2, 2021

Table 4. Results of kinetic study using 3 kinetic models: modified Gompertz, logistic and transference function

Periods	Digester	Models	CMP (Nm ³)	A (m ³)	μ (m ³ /d)	Λ (d)	R ²	Error (%)
May	Digester 1 D1	M Gompertz	53860.1	72947.9	2074	3.52	0.9990	35
		Logistic		58358.8	2253	4.75	0.9953	8.35
Transference		1819		1.46	0.9978	6.03		
May	Digester 2 D2	M Gompertz	55103.3	77640.5	2163	4.07	0.9992	40.9
		Logistic		60875.8	2361	5.34	0.9963	10.5
Transference		33459.3		1885	1.86	0.9964	39.3	
June	Digester 1 D1	M Gompertz	66288.6	89166.4	2487	1.90	0.9974	34.5
		Logistic		47245.2	2667	3.03	0.9929	9.29
Transference		86620.2		2311	0.45	0.9997	30.7	
June	Digester 2 D2	M Gompertz	64382.5	90102.8	2405	2.13	0.9976	39.9
		Logistic		71602.8	2586	3.29	0.9934	11.2
Transference		72237.9		2171	0.45	0.9997	12.2	

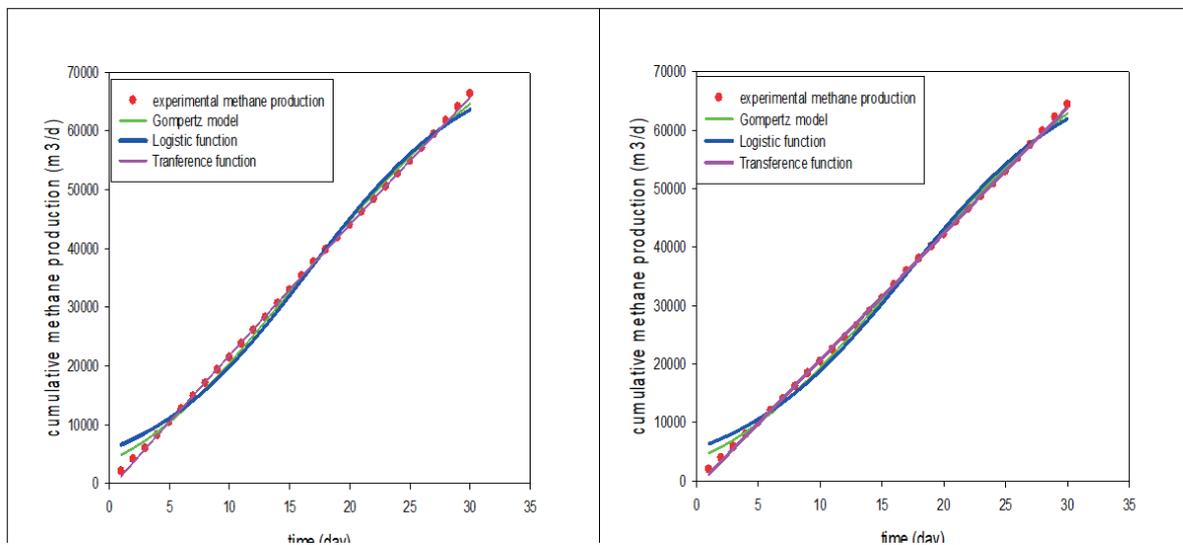


Fig. 8. Cumulative methane production and kinetic models curves as function of time for June (a) D1, (b) D2, 2021

with kinetic models curves as a function of time. As shown in the figure, the transference function curves are superposed of cumulative methane production. The curves of the logistic function and modified Gompertz model are approximated for each time of cumulative methane production. As shown in the table for the month of June, the simulated maximum methane volume (A) for Logistic and Transference function is close to the experimental cumulative methane volume (CMP). The Logistic function has a higher methane production rate compared to other models; unless it has a lower R² (Modified Gompertz has the best R²) (Table 4). For lag phase, the Transference function shows lower value compared with other model. We can conclude that the Transference function has the best fitting from experimental results by reducing the time of digestion. Same result obtained from the anaerobic digestion of date palm empty fruit

bunch which shows that the transference function has best fit for predicting kinetic parameter of producing methane (Lahboubi et al., 2022).

CONCLUSIONS

Anaerobic digestion is a process for degrading organic matter in waste into methane. The process must be followed in order to ensure that it runs in good conditions. The monitoring parameters show that the digester 1 and 2 are running in optimal conditions for the process of anaerobic digestion. The studied plants showed best results in terms of methane production for digester 1 and 2 in the order of 2356 m³/d and 2508 m³/d, respectively. The kinetics of methane production was studied by testing the experimental data of May and June, 2021 for the two anaerobic reactors

of the continuous type under mesophilic conditions of 37 °C. Three kinetic models were used to evaluate the performance of methane production: Modified Gompertz, transference functions and logistic. The three models show a good fit with the experimental data, and we can conclude that the transference function is the one that is the best adapted to the experimental results in reducing the digestion time.

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