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Study of the chemical kinetics for obtaining biogas from organic wastes (non-citrus fruit residues and cattle manure) for the validation of the design and operation of an anaerobic didactic biodigester

Estudio de la cinética química para la obtención de biogás a partir de desechos orgánicos (residuos de frutas no cítricas y estiércol vacuno) para la validación del diseño y operatividad de un biodigestor didáctico anaerobio.

Ing. Stefanie Michelle Bonilla Bermeo, Msc[1] ; Adrián Alexander Chica Mero [2] & Jamilet Viviana Vaca Chonillo [3]

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Abstract
This project is the assembly of three biodigesters (one with Agitation 43,10 L and two without it 3 L), the raw materials are the residues of non-citrus fruits (banana and papaya), inoculum and bovine manure previously homogenized and in different percentages of Concentration (manure-fruit ratio is 80:20). During the experimental phase, periodic measurements of control variables such as pH, chemical oxygen demand, temperature and solids content were carried out in the reactors. The rate of degradation is formulated as the generation of biogas in various conditions being hydrolysis the limiting stage of the process, we obtain an effluent rich in nitrogen and biogas with higher percentage in methane. The hydraulic residence time is of 24 days, based on the results of the experimental measurements and adjustments by the integral method by probing, it is obtained that the optimal mixture for the process is the mixture II, being a reaction of order $n=1$ and the kinetic constant is $k=0,0781\ d^{-1}$. The objective of the thesis project includes the study of the rate of degradation of non-citrus fruit residues and bovine manure with respect to a series of parameters mentioned above.

Key words: Biodigestor, degradation, biogas, reaction kinetics, chemical oxygen demand.

Resumen
En este proyecto se realiza el montaje de tres biodigestores (uno con agitación 43,10 L y dos sin ella 3 L), las materias primas son los residuos de frutas no cítricas (banana y papaya), inóculo y estiércol vacuno previamente homogenizadas y en diferentes porcentajes de concentración (relación estiércol-fruta es 80:20). Durante la fase experimental se efectuaron mediciones periódicas de las variables de control tales como pH, demanda química de oxígeno, temperatura y contenido de sólidos en los reactores. La velocidad de degradación se formula como la generación de biogás en diversas condiciones siendo la hidrólisis la etapa limitante del proceso, se obtiene un efluente rico en nitrógeno y biogás con mayor porcentaje en metano. El tiempo de residencia hidráulica es de 24 días, con base a los resultados de las mediciones experimentales y ajustes por el método integral por tanteo, se obtiene que la mezcla óptima para el proceso es la mezcla II, siendo una reacción de orden $n=1$ y la constante cinética es $k= 0,0781\ d^{-1}$. El objetivo del proyecto abarca el estudio de la velocidad de degradación de residuos de frutas no cítricas y estiércol vacuno con respecto a una serie de parámetros mencionados anteriormente.

Palabras claves: Biodigestor, degradación, biogás, cinética de reacciones, demanda química de oxígeno.

1. Introduction.

The increase in population and the economic growth of living standards accelerate the generation of municipal solid waste (MSW) in developing countries [1]. Considering the environmental pollution caused by the incorrect management of this waste can lead to various environmental and health problems. Generally, this waste is sent to landfills, incinerated to produce energy, composted for organic waste, and recovered (recycled). Another solution to minimize the impact of municipal solid waste is to treat the organic fraction of it through anaerobic digestion. Considering that 50-60% of MSW is biomass, characterized by a high percentage of biodegradable matter and water [2].

[1] Universidad de Guayaquil, Facultad de Ingeniería Química, stefanie.bonillab@ug.edu.ec
[2] Universidad de Guayaquil, Facultad de Ingeniería Química, adrian.chicam@ug.edu.ec
[3] Investigador independiente; chinajamilet@hotmail.com

The relevant wear of environmental circumstances over the last decades has led industries to become aware of implementing mechanisms that seek to satisfy agricultural and environmental consumption needs in a stable and efficient manner, aiming for a sustainable environment for future generations [3].

The energy obtained from fossil fuels (methane combustion is the cleanest, improving water and air quality) and biotechnology have been of great importance in environmental impact [4].

Currently, the resurgence of conventional renewable energies such as wind, hydraulic, solar, and biomass is being observed. The waste treatment methods employed do not contribute to the partial reduction of solids generated in anthropogenic activities. Among the alternative energies, we have biogas generation, which is obtained from the anaerobic degradation of organic waste [5].

Biodigesters are systems designed to optimize the production of biogas from agricultural waste, manure, or industrial effluents, allowing for the production of clean and low-cost energy through a renewable source. They offer an improved option for the treatment of organic waste, reducing the presence of contaminants, improving the fertilizing capacity of the material (compost "biofertilizer"), eliminating bad odors, and generating biogas (alternative fuel) [6]. Additionally, the utilization of biogas helps reduce greenhouse gas emissions such as methane (CH_4), which has a global warming potential 23 times greater than that of carbon dioxide (CO_2) [7]. There are various methods for obtaining methane, naturally or artificially, using biodigesters like those developed in China and India, most of which are artisanal [8].

Countries such as Germany and France use biogas as fuel for engines. In Costa Rica and other developing countries, the use of biogas is limited to direct combustion for cooking and lighting or indirect use to power internal combustion engines that generate electricity [9].

In Latin America, countries such as Bolivia, Honduras, Peru, and Ecuador have projects for developing technologies in the anaerobic digestion process. In Ecuador, until 2013, 23 family biodigesters were installed in rural areas to obtain biogas for cooking food and biofertilizer in the provinces of Guayas, Esmeraldas, Imbabura, and Cotopaxi [10].

The anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) is commonly and successfully used in industrialized countries with high-tech (sophisticated and expensive) solutions [11]. Most low-cost anaerobic digestion designs have been implemented in low- and middle-income countries for animal waste treatment. Reports on these designs are extensive, but information on the technical and operational feasibility of organic solid waste treatment is limited [5].

The anaerobic digestion process occurs within a biodigester, where biochemical and biological reactions take place due to the activation of microorganisms in the absence of oxygen, initiating three distinct phases: hydrolytic, acidogenesis, and methanogenesis. Each phase involves specific bacteria and substances responsible for substrate degradation [12]. Control parameters allow for better biogas efficiency, including strict control of temperature (directly proportional to biogas production), pH, agitation (microbial growth), and hydraulic retention time. It is estimated that the total solids percentage should be between 8-10% (wet process) or above 15% (dry process). The selection of compounds for co-digestion considers the C/N ratio, avoiding the presence of inhibitors in the process [13].

Biogas is 20% lighter than air and has an ignition temperature in the range of 650°C. It is a colorless gas that burns with a light blue flame similar to LPG. Its calorific value is 20 MJ/m3 and burns with 60% efficiency in a conventional biogas stove, with various potential uses or applications. Although the composition of biogas varies depending on the biomass used [14]. Methane gas (a component of natural gas) holds a dominant place in the global energy matrix due to its intrinsic properties, making it an optimal energy source. Its combustion generates small amounts of pollutant gas emissions (Greenhouse Gases “GHG”), making it an excellent candidate to replace gasoline in internal combustion engines [15].

This work aims to validate the design and operability of the biodigester through a kinetic study to obtain biogas from organic waste (non-citrus fruit residues and cattle manure). By applying real values obtained with weekly chemical oxygen demand, a COD vs. time graph can be created, allowing for the determination of the reaction rate constant and subsequently the order of the reaction.

2. Materials and Methods

The experimental phase will focus on the design and operability of a didactic anaerobic biodigester to obtain the chemical kinetics of anaerobic digestion from organic waste (non-citrus fruit residues and cattle manure).

2.1. Statistical Methods

Descriptive statistical methods were employed to:

a) Tabulate the selected values.
b) Examine the obtained results.
c) Display results in the form of tables.

2.2. Analytical Methods

Analytical methods will be used for the valuation and collection of each of the data obtained during the experimental phase. The analytical methods employed are:

a) Total solids content.
b) Chemical oxygen demand (COD) analysis.
c) Volatile solids content.
d) Dissolved solids.

2.3. Materials

The following tables describe the materials used both in the construction of the biodigester and in the study of the chemical kinetics of anaerobic digestion:

Table 1. Materials used in the construction of the biodigester.

Materials used in the construction of the biodigester		
Quantity	**Item No.**	**Description**
1	Small clamp	Stainless steel
3	Adaptadores de tanque de ½ in	Two PP flanges with rubbers
1	Washer Band	Rubber
1	Buflet	Rubber
2	Rubber	Rubber
1	90° Elbow	PP
1	1/2 in Shut-off Valve	Stainless Steel
1	1/2 in Shut-off Valve	Stainless Steel
1	Tarp	1.50x50 cm
1	1/2 in Pressure Gauge 0-30 psi	Aluminum, Brass
4	Butterfly Screws	Stainless Steel
1	1 hp Motor	Stainless Steel
4	Paddles	Nylon
12	Bolts	Stainless Steel
2	5-10 cm Diameter Pulleys	Stainless Steel
2	808 Bearings	Stainless Steel
1	58 L Tank	PVC
1	1/2 in Plug	Rubber
4	Teflon	PP
1	0-100°C Bimetallic Thermometer	Stainless Steel
1	1/4 in Transparent Tube	1 m LDFE
1	1 in Globe Valve	PVC

Source: (Chica, Adrián & Vaca, Jamilet, 2018)

Table 2. Materials used for the study of chemical kinetics

Materials used for the study of chemical kinetics		
Quantity	**Item No.**	**Description**
2	Agitators	Glass
4	Plastic Bottles 0.5-1 L	PET
1	Matchbox	Wood
1	Petri Dishes	Glass
6	20 ml Porcelain Capsules	Porcelain
1	Single-burner Stove	Glass
3	Serum Equipment	Plastic
2	Spatulas	Steel
4	Various Sizes Syringes	Plastic
1	Pot	Aluminum
1	Aluminum Foil	Aluminum
1	Filter Paper	Paper
1	Pear	Rubber
1	Pipette	Plastic
4	Watch batteries	Steel
2	Tweezers	Metal
6	Pipettes	Glass
6	Test tubes of different sizes	Glass
1	Liquid silicone	Silicone
6	Beakers	Glass

Source: (Chica, Adrián & Vaca, Jamilet, 2018)

3. Results

This chapter analyzes the data collected from the experimental design of each of the batch anaerobic biodigesters with and without agitation, with different concentrations for each mixture under the same environmental conditions. Through analysis, the mixture with the highest removal (conversion) percentage as well as the reaction constant and rate is determined, detecting the cause of the variation of results among each of the mixtures.

3.1. Experimental Design and Operation of the Biodigesters

Each reactor operated for 24 days, controlling sampling parameters such as temperature, pH, and motor agitation in the largest biodigester. At the end of the anaerobic biodigesters' operation period, final data were recorded as shown in Table 3. The best percentage of COD removal was observed in the second preparation. Despite having the same concentration of organic substrate as the first, its efficiency is better due to the pre-sieving of organic matter and the exclusive use of inoculum water, despite not being an agitator tank.

On the other hand, a sharp drop in pH was observed in mixture I on the fifth day, unlike the progressive drop in mixtures II and III. This was due to a minor leak in the lid of the batch anaerobic biodigester with intermittent agitation, causing a sudden drop in pH. After correcting this, a constant pH was observed until day 17, which then gradually decreased like the other mixtures, as seen in Figure 1.

Table 3. Final Results of Anaerobic Biodigesters

Property	Unit	Blend I	Blend II	Blend III
		33%	33%	31%
Initial pH	-	8	8	8
Final pH	-	6,50	6,40	6,40
Initial DQO	mg/L	150000	110000	86000
Final DQO	mg/L	60800	13002	11970
Removal DQO	%	59,50	88,18	86,01

Source: (Chica, Adrián & Vaca, Jamilet, 2018).

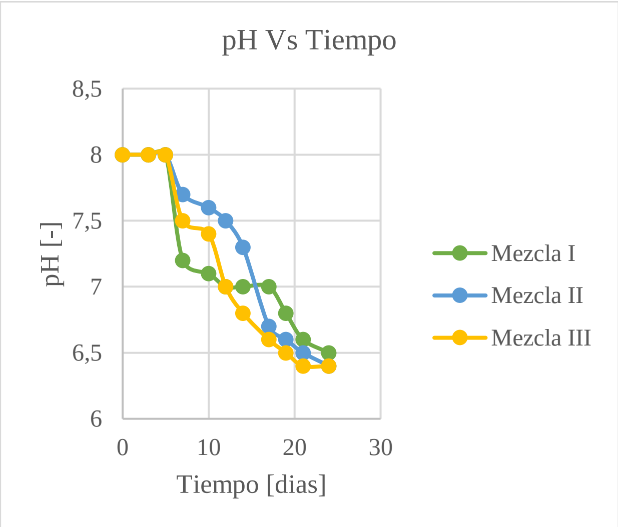

Fig. 1. pH Vs time
Source: (Chic a, Adrián & Vaca, Jamilet, 2018).

By controlling the constant temperature daily, not counting weekends in each of the biodigesters, it did not generate variations in the sampling data, thanks to the hot climate of the city of Guayaquil; However, Figure 2 shows the gas production during the operation time, as it increases every 2 or 3 days, evidenced by its extraction thanks to the manual volumetric displacement system, where mixture III, in relation to the first two, decreased the volume of methane gas production from day 10, due to the initial organic load of the non-citrus fruit substrate; while mixture II presents the highest accumulated volume of the three mixtures.

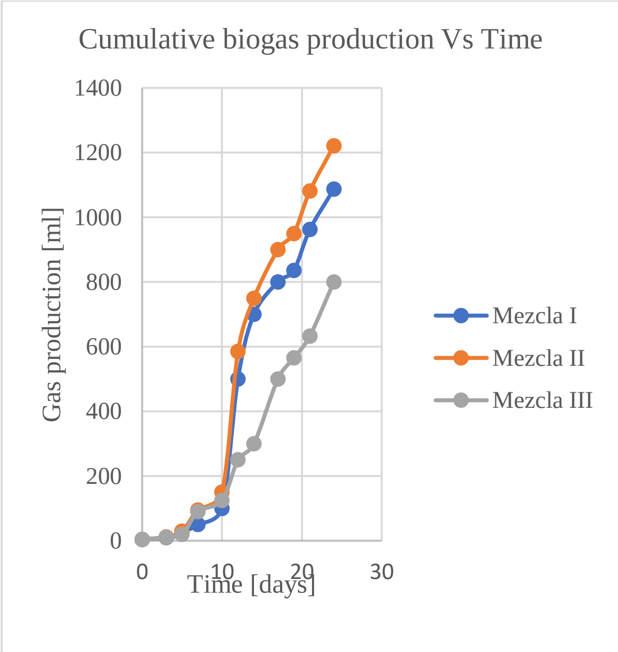

Fig. 2. Cumulative biogas production Vs time.
Source: (Chica, Adrián & Vaca, Jamilet, 2018).

3.2. Biogas characterization of the reactive mixtures

Table 4 shows how the reactive mixtures have a methane percentage higher than 70%, thanks to the inoculum and organic load prepared at the beginning; The corresponding characterization was carried out thanks to the extraction of biogas volume (100 mL of biogas for each mixture), which when bubbled in 4% sodium hydroxide gives us a percentage of pure methane, and the difference of 100% of the bubbled volume is the percentage of carbon dioxide absorbed by the sodium hydroxide solution, with mixture II being the best among all and reflected in the accumulated biogas production in Figure 2.

Table 4. Composition of biogas produced in anaerobic biodigesters.

Reactive mixture	Percentage of methane (%CH4)	Percentage of carbon dioxide (%CO2)
Blend I	75	25
Blend II	82	18
Blend III	70	30

Source: (Chic a, Adrián & Vaca, Jamilet, 2018).

After determining the composition of the gas obtained, the methane combustion test (quantitative burn analysis) was performed; it consisted of burning the methane with the help of a pilot flame (candle), forming a blue flame (conducive to CH4), then the gas obtained from the three mixtures was visualized:

Percentage of CH4 obtained from mixture I (0), mixture II (1) and mixture III (2).
Source: (Chica, Adrián & Vaca, Jamilet, 2018).

Fig. 4. Quantitative burnup analysis of the mixtures.
Source: (Chica, Adrián & Vaca, Jamilet, 2018).

3.3. Investigation of the Optimal Mixture in Batch Biodigesters Without Feeding

The preparation of the initial mixtures for the batch biodigesters without feeding (with and without agitation) contributes to the determination of the optimal mixture for the anaerobic digestion process. This preparation was based on the adjustment of two parameters: the variation in the percentage of non-citrus fruit residues and control parameters such as temperature and agitation.

The operating volume of the biodigesters varies; the biodigester with agitation was designed for an operating volume of 43.10 L, while the others were designed for 3 L. These biodigesters operated over a period of 24 days, during which the accumulated volume of biogas produced was analyzed. The selection of the optimal mixture was based on the quantity of biogas produced, considering its composition (higher percentage of CH4).

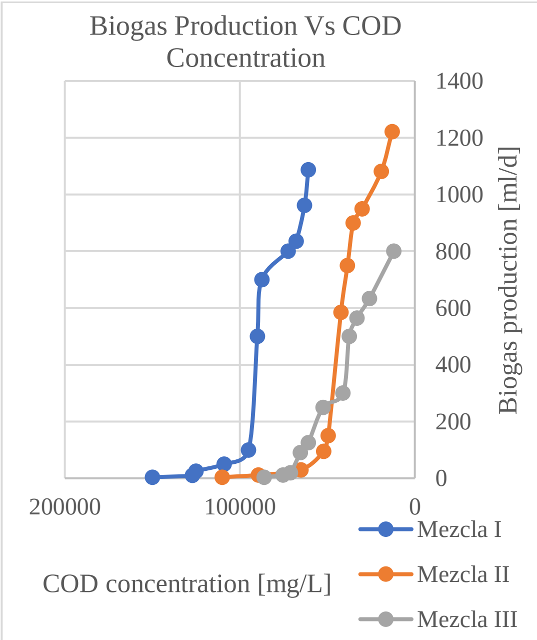

Fig. 5. Biogas production Vs COD concentration.
Source: (Chica, Adrián & Vaca, Jamilet, 2018).

When comparing the biogas production Vs decrease in COD concentration as visualized in Figure 5, the optimal mixture is determined by the different COD removal percentages within the same time frame having the highest percentage concentration of organic substrate with better homogenization with particle sizes of 0.02 mm."

3.4. Adjustment to the Monod equation.

Adjusting the collected data to the Monod equation according to equation 30 we can obtain the mathematically linearized equation to obtain the Monod constant and the cellular growth constant, as presented below:

$$\frac{1}{C_A}=\frac{k_c}{K_s}t-\frac{1}{K_s} \qquad (1)$$

Where:

C_A: Concentration of COD $\left[\frac{mg}{L}\right]$

k_c: Constante de crecimiento celular $\left[d^{-1}\right]$

K_s: Cellular growth constant [mg/L]

t: Tiem [d]

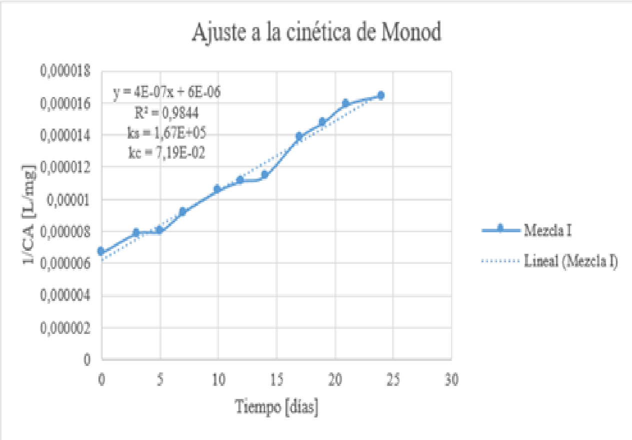

Fig. 6. Fit to Monod kinetics for mixture I.
Source: (Chica, Adrián & Vaca, Jamilet, 2018).

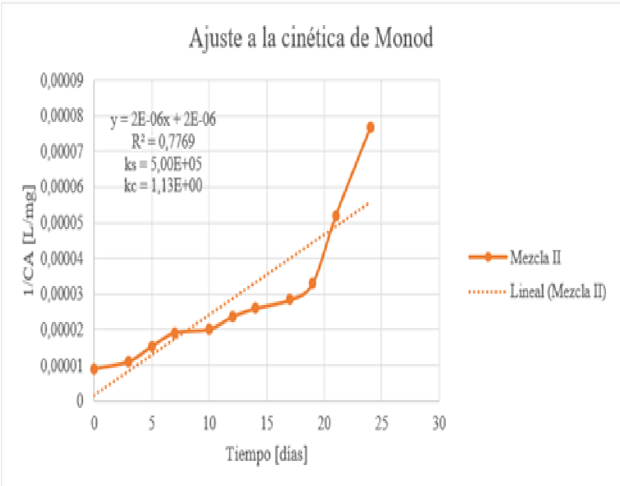

Fig. 7. Fit to Monod kinetics for mixture II.
Source: (Chica, Adrián & Vaca, Jamilet, 2018).

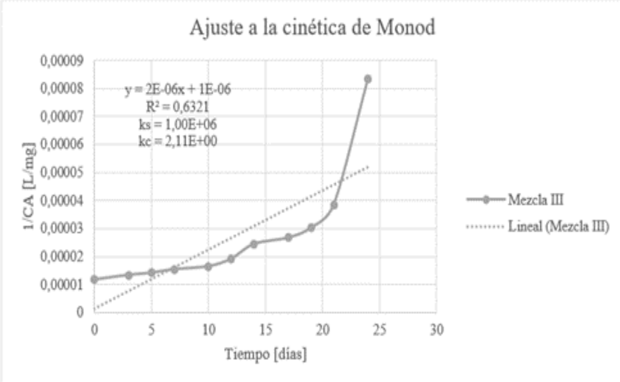

Fig. 8. Adjustment to Monod kinetics for mixture III.
Source: (Chica, Adrián & Vaca, Jamilet, 2018).

The analysis shows that the data from mixture I have a better adjustment to the trend line due to its determination coefficient, but mixture III has higher Monod constants than the three mixtures, confirming by choice that mixture II is the most accepted and optimal due to its average adjustment to Monod kinetics as observed in Figures 6, 7 and 8.

Table 5. Values of the kinetic constants of the Monod equation.

Constants	Units	Blend I	Blend II	Blend III
K_s	$\left[\frac{mg}{L}\right]$	1,67E+05	5,00E+05	1,00E+06
k_c	$[d^{-1}]$	7,19E-02	1,13	2,11

Source: (Chica, Adrián & Vaca, Jamilet, 2018).

4. Conclusions

To obtain values that contribute to the kinetic study of the anaerobic digestion of non-citrus fruit waste and bovine manure, a didactic anaerobic biodigester of complete mix (with agitation) was designed, with an operating volume of 43.10 L (total tank capacity of 58 L) prior to the kinetic study for its respective validation in comparison with discontinuous biodigesters without agitation, with an operating volume of 3 L (container capacity of 4 L). Due to the complexity of handling the operating volume of the biodigester, the formulation was replicated with prior sieving and varying the percentage of fruit substrate concentration in the modified containers. Thanks to the hydrostatic tests carried out, the biodigesters are sealed with a margin of error observed in the first five days, where the minimal gas leak produces a delay in the hydrostatic stabilization of the anaerobic process, as evidenced by the control parameters (pH, COD, etc.) analyzed periodically.

The main control parameters influencing bacterial growth were temperature, pH, agitation, alkalinity, and the C/N ratio. The initial manure-to-fruit ratio was 80:20. Temperature and pH were rigorously controlled, with agitation occurring at four-hour intervals (prior to sample extraction). The temperature was maintained at around 30°C with the help of a thermal jacket. The pH progressively decreased to the established range (8-6.40), resulting in a continuous reduction in COD without alterations or interferences during the operational period.

The kinetic study of the anaerobic digestion of the specific organic substrate is based on the degradation of COD during the biodigester's operation. By applying the integral method, the collected data fit the trend line reflected in the R^2 closest to one, resulting in a first-order kinetics under the same environmental conditions for each reactor with a different operational formulation applied to each mixture. It was concluded that the kinetic constant is strictly related to the linear adjustment of the applied method and its determination coefficient (the kinetic coefficient and the determination coefficient are inversely proportional to the order applied in the integral method). The resulting values of the kinetic constant were 0.039 d^{-1} (mixture I), 0.0781 d^{-1} (mixture II), and 0.0696 d^{-1} (mixture III) with first-order for each mixture, considering mixture II as the optimal one. Due to the experimental design for an anaerobic biodigester without continuous feeding, the COD concentration values yielded a negative slope with an R^2 value not approaching one (0.17) when applying the differential method. It was concluded that the differential method is not applicable for discontinuous experimental designs with a 24-day operational and hydraulic retention period, without generalization of experimental replication to obtain initial values for each experiment (biodigesters with continuous feeding).

The degradation rate in the anaerobic biodigester, both with and without agitation, was analyzed in relation to the operational period. It was observed that mixture II had a superior reaction rate due to its high COD concentration removal rate during the first five days, followed by a progressive decrease similar to the other mixtures. It was concluded that the reaction rate depends on the concentration of organic matter from bovine manure and non-citrus fruit residues, free of inorganic material (stones, soil, etc.), as reflected in the COD analysis. Additionally, the immediate stabilization of the organic substrate within a hermetically sealed biodigester, with strict control of parameters (temperature, pH, COD, etc.), is crucial to avoid minimal leaks. Continuous oxygen ingress delays the stabilization phase of the organic matter for biogas production.

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