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Kinetics and methane generation potential from dog waste through anaerobic digestion

Cinética e potencial de geração de metano de dejetos de cães através de digestão anaeróbia

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ABSTRACT

The high and growing number of dogs present in the urban environment and the consequent generation of dog waste (DW) has as a problem the emergence and spread of zoonotic diseases due to inadequate disposal in effluent treatment systems, sanitary landfills, and urban drainage. Disposal of these wastes is often neglected due to the false perception of low impact when evaluating the quantities generated in a single household. An option for the treatment of these residues is anaerobic digestion (AD) with the consequent production of methane (CH_4). This study determined the methane generation potential of DW, also testing the influence of the use of sodium bicarbonate ($NaHCO_3$) as alkalizing AD in residue tests in addition to bicarbonate (DWb). The methane potential resulted in 99.63 $NmL.gVS^{-1}$ (DWb) and 123.79 $NmL.gVS^{-1}$ (DW). The insertion of sodium bicarbonate (NaHCO3) did not present an advantage in terms of improvement in the methane generation potential or the concentration of methane in the biogas. Five kinetic models were tested, all of which were compatible with the experimental data obtained. However, the Cone model was the one that presented the best fit for all configurations (DWb and DW) tested.

Palavras-Chave
modelos cinéticos
resíduos de animais
potencial de metano
valorização energética
biogás

RESUMO

O elevado e crescente número de cães presentes no meio urbano e a consequente geração de dejetos caninos (DW) tem como problema o surgimento e disseminação de doenças zoonóticas devido ao descarte inadequado em sistemas de tratamento de efluentes, aterros sanitários e drenagem urbana. A destinação desses resíduos é muitas vezes negligenciada devido à falsa percepção de baixo impacto ao avaliar as quantidades geradas em uma única residência. Uma opção para o tratamento desses resíduos é a digestão anaeróbia (DA) com a consequente produção de metano (CH_4). Este estudo determinou o potencial de geração de metano de DW, testando também a influência do uso de bicarbonato de sódio ($NaHCO_3$) como alcalinizante DA em testes de resíduos em adição ao bicarbonato (DWb). O potencial de metano resultou em 99,63 $NmL.gSV^{-1}$ (DWb) e 123,79 $NmL.gVS^{-1}$ (DW). A inserção de bicarbonato de sódio ($NaHCO_3$) não apresentou vantagem em termos de melhoria no potencial de geração de metano ou na concentração de metano no biogás. Foram testados cinco modelos cinéticos, todos compatíveis com os dados experimentais obtidos. No entanto, o modelo Cone foi o que apresentou o melhor ajuste para todas as configurações (DWb e DW) testadas.

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Introdução

Municipal solid waste is classified into several types, among these, organic solid waste, from the organic matter, can be destined for composting or anaerobic digestion in a way that allows the reuse of biosolids generated for recovery of impacted soils or agricultural use.

Thus, among the solid waste generated by a population, it is known that waste from domestic animals fit into the category of organic matter. The number of animals, types and sizes has been expanding in urban centers, as well as the growing interest of people in incorporating them into their routines as part of urban culture and modern modus operandi. Daily huge amounts of waste from these animals are generated, either dispersed (in houses or streets) or concentrated (in veterinary clinics, kennels, and society organizations aimed at rescuing those abandoned on the thoroughfares.

The number of dogs in Brazil is quite expressive and reflects the current lifestyle of the population, where domestic animals are increasingly present in the homes of the country. This phenomenon has generated the need for greater care of animals, including their dog waste (DW) since their mismanagement leads to health problems.

Many zoonotic diseases (DOS PASSOS; MARTINS, 2020), such as COVID-19 (Sars-CoV-2) (MACEDO JUNIOR, 2020), arise through anthropic impacts on animals and nature (ZANELLA, 2016). In general, diseases such as rabies (dogs and cats), toxoplasmosis (birds), and leptospirosis (rodents) (SANTOS; BRAGA, 2021) are more commonly visualized.

The residue from the physiological needs of animals, called waste, usually when produced in the urban environment, is treated as common urban solid waste, that is, is deposited, most often, in dumps or landfills, and can be directed to sanitary effluents, causing the dispersion of zoonotic diseases. For the management of these animals waste, they have as an alternative their treatment through biodigesters, resulting in biosolids and biogas as final products (PENTEADO et al., 2018).

The anaerobic digestion process consists of treatment for the reduction of organic and pathogenic load, when, in the end, renewable energy is obtained from biogas (source of heat/energy) and digested sludge (biofertilizer), which is presented as a nutrient-rich product, and prone to use in the agricultural sector (LIN et al., 2018).

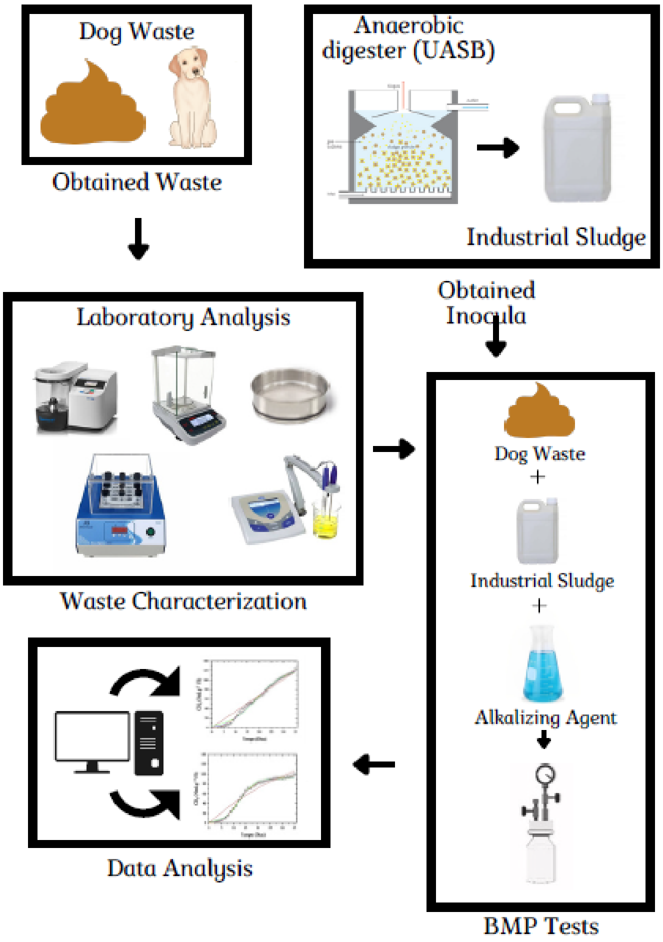
However, there is a need to observe the presence of pathogens found in the sludge digested from animal waste, since these, when disposed of in the soil, can lead to zoonotic diseases. For this, there is an estimate through laboratory tests such as the Biochemical Methane Potential (BMP), in which the specific methane production is calculated using inoculum and substrate (GUERI et al., 2018). Thus, with the effects of methane generation potential, it is possible to determine several parameters, such as kinetics, which serve to size reactors of large size and specificity, generating better anaerobic digestion results.

Along these lines, the objective of this research was to evaluate, quantitatively and qualitatively, the potential of biogas and methane generation from the anaerobic digestion of dog waste, for energy recovery purposes, through the Biochemical Potential of Methane (BMP) test.

Materials and methods

Figure 1 presents the methodological sequence adopted by this work. Details will be presented in the following items.

Figure 1. Methodological sequence adopted by this work



Source: Authors (2023)

Obtaining dog waste and anaerobic granular sludge

The sample of substrate *in natura*, dog waste (S was obtained from the Pernambuco Fire Department Kennel, located in the municipality of Abreu e Lima, in the State of Pernambuco, Brazil. Before performing the characterization tests, the substrate was taken to the oven at a temperature of 65 ± 2 °C for drying until moisture stabilization, then it was crushed, sieved (20 mesh sieve), and stored at room temperature in plastic pots.

It used an anaerobic inoculum, anaerobic granular sludge (I), obtained from a real-scale UASB (anaerobic up-flow Sludge Blanket) reactor, which used vinasse as substrate. Samples of 10 liters of anaerobic inoculum were collected, which were packed in polyethylene canisters and stored under refrigeration (4 ± 1 ºC), before the tests.

Characterization of substrate and inoculum

The substrate (S), dog waste, the inoculum (I), anaerobic granular sludge, and the content of the initial and final BMP test were characterized by analysis of hydrogen potential (pH), electrical conductivity (EC), solids, moisture according to WHO (1978)), elemental analysis (carbon, nitrogen, sulfur, and hydrogen) total alkalinity (TA) (KAPP, 1984) and fiber content (lignin, hemicellulose, and cellulose) Van Soest (1994). All analyses were performed in triplicate.

Biochemical Methane Potential (BMP) test

The methodology used for the Biochemical Methane Potential (BMP) test was based on Silva et al. (2019). The BMP test is performed in batches, using glass (borosilicate) flasks with a volume of 250 mL, composed of closed nylon lids and sealing rings.

The lid of this reactor consisted of two needle valves, one serving to relieve the resulting pressure in the test or for the insertion of N_2 (O_2 purge at the beginning of the test), and another where a 100 kPa mechanical manometer was installed for measuring the pressure of the biogas in the reactor.

The substrate (S) and inoculum (I) inserted in each reactor was equivalent to 5 g and 50 g, on average, with the addition of distilled water to result in a final headspace of 20% of the total volume of the reactor, that is, in 50 mL. The amount of sodium bicarbonate ($NaHCO_3$) totaled 1 g, for some configurations.

The experiment was carried out in triplicate, still analyzing the blanks, where it was considered only the insertion of distilled water and inoculum.

The reactor was filled in according to the methodology of Silva et al. (2019), following the sequence: insertion of the inoculum into the reaction flask (BMP), the addition of sodium bicarbonate in the distilled water, insertion of the substrate into the reaction flask (BMP), manual mixing of the reaction medium, measuring the pH of the reactor mixture after 1 minute of inoculum/substrate settling, N_2 recirculation, closing the reactor and valves, and finally, wrapping the reactor in aluminum foil.

Then, the gas outlet and inlet valves were closed, and the manometers were reattached to the reactors maintaining pressure in all 20 KPa flasks (SANTOS et al., 2020). After that, the reactors were kept on an incubator (TECHNAL TE 424) with temperature control (37 ± 2° C) and with orbital agitation (60 rpm) for 35 days.

The volume of accumulated biogas was calculated indirectly by reading the pressure indicated on the manometers of the reactors, and daily monitoring was performed, according to the methodology of Ivanova et al. (2008).

The composition of biogas (CH_4 and CO_2) was evaluated from the third day of the experiment by gas chromatography (HP 5890), with a thermal conductivity detector (TCD) and analytical separation on a Porapak "N" column (6m long, 2.5 mm internal diameter, and 3µm thick stationary phase), using H_2 as a carrier gas, at an oven temperature of 80ºC. The analytical standard used 60% CH_4 and 40% CO_2.

Potential generation and production rate of biogas and methane

The calculation of potential generation (Ym) was given in Equation 1 with a unit of measurement in $NmL.g^{-1}$ VS of the residue. The net volume resulted from the difference of the accumulated volume by the biogas/methane of the substrate with the inoculum (VAs) by the accumulated volume of the blank (B) of the respective inoculum (VAi), divided by the mass of the waste (in gram volatile solids) according to Equation 1. The potential generation calculation (Ym) is performed by Equation 1.

$$Y_m = \frac{VA_S - VA_i}{VS_g} \qquad \text{(Eq.1)}$$

Where:
Ym = Potential of biogas or methane ($NmL.g^{-1}VS$)
VAs = Accumulated volume of biogas/methane of the studied configuration (NmL)
VAi = Cumulative volume of biogas/methane of the inoculum blank (NmL)
VSg= Initial VS concentration of dry substrate ($g^{-1}VS$)

In Equation 2 the biogas generation rate (daily) was presented.

$$T_{biogás} = \frac{\Delta V_{biogas}}{\Delta T_{1-0}} = \frac{V_{biogas\,t1} - V_{biogas\,t0}}{T_1 - T_0} \qquad \text{(Eq.2)}$$

Where:
T_{biogas} = Daily biogas or methane generation rate ($NmL.d^{-1}$)
$VA_{biogas\ t1}$ = Produced volume of biogas/methane accumulated on day 1(NmL)
$VA_{biogas\ t0}$ = Produced volume of biogas/methane accumulated on day 0 (NmL)
T_1 = Time 1(d)
T_0 = Time 0 (d)

Kinect models

The kinetic analysis was performed using the OriginPro 8.0 software, through the adjustments of exponential curves and nonlinear regression (ABU-REESH, 2014; MORAES et al., 2021) of the results of methane potential obtained experimentally.

Five kinetic models were tested: Modified Gompertz (Eq. 3), First-order (Eq. 4), Cone model (Eq. 5), modified Logistic model (Eq. 6) and Fitzhugh model (Eq. 7).

$$y(t) = y_m \cdot exp\left(- exp\left(\frac{\mu \cdot e}{y_m}(\lambda - t) + 1\right)\right) \qquad \text{(Eq.3)}$$

$$y(t) = y_m(1 - exp(- k \cdot t)) \qquad \text{(Eq.4)}$$

$$y(t) = \frac{y_m}{1 + \left(k_{hyd} \cdot t\right)^{-n}} \qquad \text{(Eq.5)}$$

$$y(t) = \frac{y_m}{1 + exp\left(\frac{4 \cdot \mu}{y_m}(\lambda - t) + 2\right)} \qquad \text{(Eq.6)}$$

$$y(t) = y_m\left(1 - exp(- k \cdot t)^n\right) \qquad \text{(Eq.7)}$$

Where:
y(t) is methane cumulative production (NmL.g^{-1} VS), t is experimental execution time (d), k is hydrolysis constant (d^{-1}), refers to methane maximum production (NmL.g^{-1} VS), is maximum methane production rate (NmL.d^{-1}), and is lag phase (d).

Data Analysis

The potential of the proposed models was measured by comparing the experimental and predicted values. For this purpose, the residual sum of squares (RSS) (Eq. 8) and the determination factor (R^2) (Eq.9) were calculated. In which, is the predicted value and is the measured value.

$$RSS = \sum_{i-1}^{N} \left(Z_{f_i} - Z_{o_i}\right)^2 \qquad \text{(Eq.8)}$$

$$\boldsymbol{R}^2 = \left(\frac{\sum(\boldsymbol{Z}_{f_i} - \overline{\boldsymbol{Z}_{f_i}})(\boldsymbol{Z}_{o_i} - \overline{\boldsymbol{Z}_{o_i}})}{\sqrt{\sum(\boldsymbol{Z}_{f_i} - \overline{\boldsymbol{Z}_{f_i}})^2 \sum(\boldsymbol{Z}_{o_i} - \overline{\boldsymbol{Z}_{o_i}})^2}}\right)^2 \qquad \text{(Eq.9)}$$

Results and discussion

Characterization of dog waste and anaerobic granular sludge

Table 1 present the characterization results in terms of pH, AT, moisture, EC, elemental analysis, solids, and fiber, referring to the substrate (S), dog waste, and inoculum (I), anaerobic granular sludge.

It is worth noting that for the characterization of the substrate (S), few literature studies were evidenced in a specific way for the topic, during the period from 2000 to 2022.

The most found parameters were pH, EC, elemental analysis, moisture, and total solids.

Table 1. Characterization of the dog waste and inoculum

Analysis	Dog waste	Inoculum
pH	7.58 ± 0.11	7.7± 0.2
TA (mg $CaCO_3$/L)	3103,47 ± 123.38	-
Moisture (%)	67.44± 2.55	89.4± 0.1
EC (mS/cm)	7053,78 ± 461.70	-
TOC (%)	54.96 ± 8.97	-
TN (%)	0.05 ± 0.01	-
EH (%)	0.0004 ± 0.0003	-
S (%)	2.64 ± 1.64	-
TS (%)	32.56 ± 2.55	10.5 ± 0.2
FS (%)	22.55 ± 3.13	-
VS (%)	77.45 ± 3.13	75.9 ± 0.3
Lignin (%)	0 ± 0	-
Hemicellulose (%)	1.40 ± 0.52	-
Cellulose (%)	0 ± 0	-
C/N	-	8.95

Legend: COD: Chemical oxygen demand; TOC: Total organic carbon; TN: total nitrogen; EC: Electrical conductivity; EH: Extractable hydrogen; S: Sulfur; TS: Total solids; FS: Total fixed solids; VS: Total volatile solids; TA=Total alkalinity; C: carbon; N: nitrogen.

The pH of the S located in this research corresponds to 7.58. Other works found values of 6.33 (URREGO, 2017) and 5.9 (MARTÍNEZ-SABATER et al., 2019) for dog waste.

The inoculum (I) obtained a pH in the neutral range (6.5 to 7.5) equivalent to 7.7, being within the average, exposed by some authors, for granular sludge inoculum (7.6-8.6) (PARRA-OROBIO et al., 2018; VALERO et al., 2020).

The EC of the S presented an average value of 7.054 ms.cm^{-1}. When compared to the study of Martínez-Sabater et al. (2019), a lower value for the EC was verified, equal to 5.900 ms.cm^{-1}. Such a result may be related to issues concerning animal metabolism or the food ingested by it.

The elemental analysis of the S refers to Total Organic Carbon (TOC), Total Nitrogen (TN), Extractable Hydrogen (EH), and Sulfur (S), obtaining average results of 55%, 0.062%, 0.0004%, and 0.37%, respectively. Other works identified results of 43.5% for TOC (MARTÍNEZ SABATER, 2019) and 0.175% for TN (OKOROIGWE et al., 2014), similar values to those obtained in this study. However, a higher value for TN, corresponding to 0.7%, was observed in the work of Nemiroff and Patterson (2007).

As previously mentioned, referring to other parameters, low TN values may be related to the type of food used in the kennel, because it is a premium feed, where nutrients are available with optimized metabolic values. Angelidaki et al. (2009) reported that values above 80% demonstrate the behavior of high biodegradability and good functioning in anaerobic systems. Concerning I, the volatile solids content presented a percentage of 75.9%. A similar result was found by Oliveira et al. (2018) and Santos Filho et al. (2018) for VS (63%).

The higher concentration of is related to the substrate characteristic because it has a variability of toxic elements in its composition, changing the sludge particle size, granulation process, and active biomass concentration in the granules (VS).

The substrate moisture value reached 67.44%, similar of Okoroigwe et al. (2014) whose result attained 75%. In terms of moisture content (>80%) of the inoculum, the values were close to those found in the literature on anaerobic sludge (Silva et al., 2021; Valença et al., 2021). The C/N ratio of the GS was also within the typical range (between 5.0 and 11.0) where a value of 8.95 was found, which favors equilibrium in anaerobic reactors (SANTOS et al. 2020).

The S presented low values for fiber content, founding the percentage of lignin, hemicellulose, and cellulose, in the values of 0%, 1.40%, and 0%, respectively, which demonstrates to be a lignocellulosic substrate of easy due to the low concentration of lignin and hemicellulose that act as a physical barrier, facilitating the conversion of biomass into fermentable sugars (ANGELIDAKI et al., 2009; DOLLHOFER et al., 2015). This factor can be justified by the type of feeding ingested by these animals, that is, the use of dog feed with low fiber content, resulting in a higher digestibility coefficient (AFONSO et al., 2021).

Regarding the reactional contents of the reactors, these were analyzed after 35 days for the parameters: pH, TA, VFA, VFA/TA, and EC whose average results are presented in Table 2. The final values of the DWb and Bb (with bicarbonate) configurations showed a slightly higher average pH than the DW and B (without bicarbonate).

The results showed similarity to those found by Okoroigwe et al. (2014), in the range of 6.36 to 7.78; this is considered close to the ideal range, of 6.6 and 7.4, for the development of methanogenic arches (CHERNICHARO, 2008).

Table 2. Characterization of final reaction contents of BMP tests

Configuration	pH	TA ($mg.L^{-1}$)	VFA ($mg.L^{-1}$)	VFA/TA	EC ($mS.cm^{-1}$)
DW	6.93 ± 0.03	3620,00 ± 213.33	697.65 ± 468.45	0.202 ± 0.148	7.48 ± 0.004
DWb	7.28 ± 0.01	6549,33 ± 126.22	391.12 ± 28.51	0.060 ± 0.003	11.58 ± 0.258
Bb	7.51 ± 0.06	4144,00 ± 104.00	140.01 ± 98.67	0.033 ± 0.023	7.20 ± 0.041
B	7.10 ± 0.01	860.00 ± 10.67	90.14 ± 6.84	0.105 ± 0.008	2.11 ± 0.018

Legend: TA = Total alkalinity; VFA = Volatile fatty acids; DW = Dog waste without bicarbonate; DWb =Dog waste with bicarbonate; B = blank without bicarbonate; Bb = blank with bicarbonate; EC: Electrical conductivity

When comparing the alkalinity of the reactors, these showed higher values for the DWb and Bb configurations concerning the DW and B configurations. In this case, DWb proved to be outside the ideal standard that, according to Bajpai et al. (2017) ranges between 1000 to 5000 mg. L^{-1} to maintain the acidification of the reactor from the acid formation. This behavior is similar conductivity analysis.

It was observed that the VFA for the DWb configuration (391 mg. L^{-1}) showed lower values than DW (697.65 mg. L^{-1}), indicating the influence of bicarbonate positively, causing there to be the stability of the reaction medium, to drive higher consumption and non-accumulation of VFA in the rational medium. This fact is evidenced when the relation of VFA/TA is observed.

The final VFA/TA ratio of the BMP tests of the evaluated configurations (DW, DWb, Bb and B) was less than 0.4, indicating the high stability of the process during the experiment.

According to Liu et al. (2012), the VFA/TA ratio should be less than 0.4, indicating stability of the anaerobic reactor, with no risk of acidification during the process.

The final EC (2.11-7.48 mS.cm-1) of most configurations was within the ideal range (2.9–7.7 mS.cm-1) for methane production recommended by Alcântara (2007).

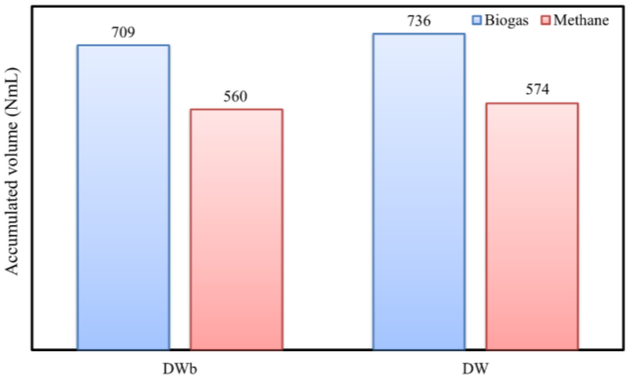
Cumulative production, generation rate, percentage of methane in biogas, and generation methane potential

According to Figure 2, in terms of average accumulated biogas production, the DW configuration (736 NmL) presented a higher volume of biogas compared to DWb (709 NmL).

As concerns, the average accumulated methane volume, the DW configuration (574 NmL) pointed out a higher result when compared to DWb (560 NmL). It was observed that the DWb configurations presented a result (average) of a little lower in terms of the volume of biogas and methane accumulated concerning the DW ones.

It is reported in the literature that for residues that have adequate initial TA and pH characteristics for AD, in the order of TA=1000-5000 mg. L^{-1} (GERARDI, 2003; METCALF AND EDDY, 2016) and pH 6.5-7, 5 (OLIVEIRA et al., 2018; Lee et al., 2019), the addition of more alkalizing agent can have a negative effect.

Figure 2. The accumulated volume of biogas and methane in the configuration



Legend: DWb: Dog waste with bicarbonate; DW: Dog waste without bicarbonate.

The literature reports that TA values above 5000 mg. L^{-1} can led to a significant reduction in biogas production. When in solution, the Na^+ ions present in the alkalinizer ($NaHCO_3$) can lead to an inhibitory effect. McCarty (1964) indicates that Na^+ concentrations between 100 and 200 mg/L are stimulant, 3500–5500 mg. L^{-1} moderately toxic, and above 8000 mg. L^{-1} inhibitory and toxic to AD. Oh et al. (2008) reported a 50% loss in CH_4 production due to sodium for food waste AD inhibition (4.6 g $Na^+.L^{-1}$). Lee and Hwang (2019) and Lee et al. (2021) reported in addition to the inhibition of methane production and delay in the lag phase (λ).

The introduction of a more alkalizing agent can interfere in the volumetric production of biogas, probably due to a bacteriostatic effect. Excess alkalinity can be detrimental to microorganisms, causing the disintegration of microbial granules and subsequent process failure (SANDBERG; AHRING, 1992; FRANKE-WHITTLE et al., 2014).

The high amount of Na^+ can interfere with cellular osmotic pressure and can destroy granular structures, making it difficult to mass transfer of metabolic by-products between species in the granular structure, or even lead to the loss of part of more sensitive microbial species (no less important to AD). It is observed in Table 2 that in terms of the TA of the final content of the BMP, for the DWb configurations, the average TA was above the recommended value (6549.33 ± 126.22 mg. L^{-1}), which may corroborate this idea.

It is noteworthy for the results obtained pointed to the non-need use of the alkalizing agent in the AD of this residue, which is a positive highlight given the cost and operational issues.

In the same way when we observe the relation between the accumulated biogas volumes and the daily biogas production rate, we found that bicarbonate also had a negative influence on these two parameters for the DWb (3A) and DW (3B) configurations (with and without bicarbonate, respectively) (Figure 3).

The configurations DWb (Figure 3A) also had an extension of the initial degradation phase about the configurations DW (Figure 3B), influencing in the end the total stabilization time of the substrate. The assumptions of the bacteriostatic effect caused probably by the Na^+ of bicarbonate are the same as those discussed in the analysis of Figure 3.

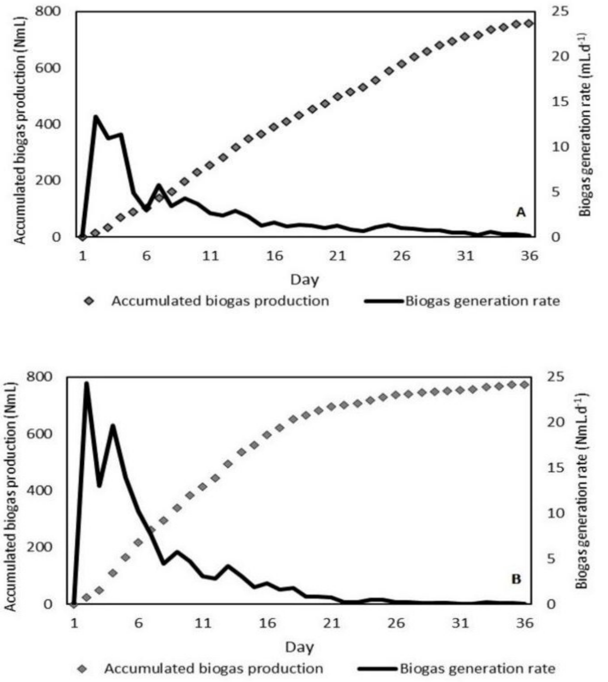
In Figure 4 we can see the average concentrations of CH_4, and CO_2 obtained in the DW and DWb configurations. When observing the average composition (4 samples in triplicates of each test) of the biogas obtained in the DW and DWb configurations, it was observed that in terms of average results there was no significant difference in the concentration of biogas obtained in the two configurations.

This high concentration of methane was probably related to the very nature of the substrate (S), which is highly biodegradable (low amount of cellulosic material).

The high amount of methane is a positive factor in the case of energy recovery of this waste. It was also observed a high concentration of methane obtained (>78%), higher than that of other animal residues such as pigs, chickens, and cows, commonly reported in the literature (50-70% as CH_4) (COLATTO; LANGER, 2011; SANTOS; NARDI JUNIOR, 2013).

These differences are probably associated with the contents of hemicellulose material (higher in these residues).

Figure 3. Rate of daily biogas generation and total accumulated biogas and methane for dog waste with bicarbonate (A) and without bicarbonate (B).

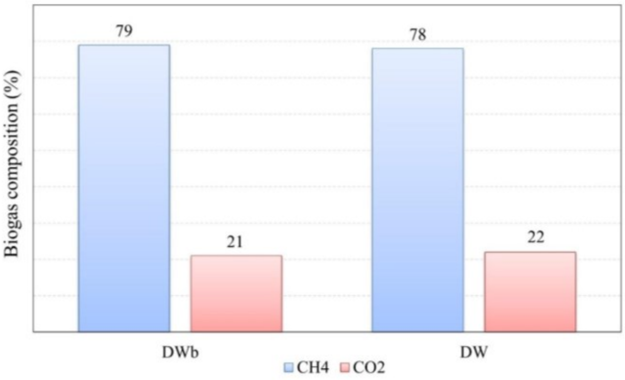


Legend: A: DWb (Dog waste with bicarbonate); B: DW: Dog waste without bicarbonate.

The bicarbonate effect had a more significant influence on the generation rate, but not on the quality of the biogas generated, indicating that there was no toxic effect on the methanogenic groups of microorganisms, which may have been more significant in the hydrolysis phase.

DW had the best methane potential (124 NmL. CH_4g^{-1}.VS) compared to the DWb configuration (99. NmL. CH_4g^{-1}.VS). The methane generation potential obtained is comparable to other animal waste such as those from horses, chickens, and pigs, being therefore usable for anaerobic digestion as a substrate.

Figure 4. Average CH_4 and CO_2 concentrations obtained in the configurations.



Legend: DWb: Dog waste with bicarbonate; DW: Dog waste without bicarbonate.

The methane potential obtained is within the range (112 to 326 NmL.g^{-1} VS) found by Carabeo Pérez et al. (2021) when studying the co-digestion of the horse, rabbit, and goat manure with the addition of inoculum in

0.5 L batch reactors under controlled temperature (35 ± 2 °C) for 40 days.

Similar results of methane potential (86 to 102 $NmL.g^{-1}$ VS) were also obtained by Silva et al. (2021) when studying the digestion of quail and chicken waste with the addition of granular sludge under mesophilic conditions (37ºC).

However, Rodriguez et al. (2017) evaluated the digestion of pig manure with the addition of sewage sludge, in BMP tests they obtained a methane potential greater than 437 $NmL.g^{-1}$ VS at a temperature of 32ºC. Despite the similarities of the potentials obtained by different authors, each residue has its physicochemical characteristics that will depend on the animal physiology and the eating habits imposed on the animals in its handling.

The methane production will be influenced by the experimental conditions applied in the BMP tests (pre-treatments, alkalizing addition, type of inoculum, etc). The results of the generation potential similar of other animal species corroborate its potential use for this purpose.

It is noteworthy, however, that its application in large-scale practice becomes more suitable for places where there are large concentrations of these animals such as kennels, veterinary hospitals, and large breeding sites. In this case, health and sanitary aspects must be considered as a priority to the issue of energy recovery, since the proper treatment of these residues reflects the risks of zoonotic diseases dispersed in the environment.

Kinect Models

Figure 5 are presented the adjustments of the experimental data of the two configurations (DW and DWb) to the 5 kinetic models studied: Where (A) - DW + 1st order kinetics; (B) - DWb + 1st order kinetics; (C) - DW + Logistics; (D) - DWb + Logistics; (E) - DW + Modified Gompertz; (F) - DWb + Modified Gompertz; (G) - DW + Fitzhugh; (H) - DWb + Fitzhugh; (I) - DW + Cone; (J) - DW + Cone. The two configurations studied (DW and DWb) showed excellent fits for all studied kinetic models.

Table 3 presents the details of the kinetic and statistical parameters of the 5 kinetic models evaluated for the two configurations studied (DW and DWb). Furthermore, the correlation coefficient (R^2) of the configurations indicated a variation of 0.933 to 0.998; while the value of the residual sum of squares (RSS) indicated a variation of 81,5 to 2882.0, where the smallest parameter shows which is the ideal kinetic model to be used in the studied configuration. Therefore, the lowest RSS value for DWb (233.6 $NmL.g^{-1}$ VS) and DW (81.5 $NmL.g^{-1}$ VS) was the Cone model for both and is considered the most efficient kinetic model for the adjustment of methane production.

The k value for DW was equivalent to 0.0000997 d^{-1}, 0.037 d^{-1} e 0.00000586 d^{-1}, and for DWb it corresponds to 0.025 d^{-1}, 0.080 d^{-1}, and 0.161 d^{-1}, both for the CH_4 kinetics curves referring to the first-order, Cone and Fitzhugh models, respectively, the Cone Model Fitzhugh Model for the two configurations (DW and DWb) being the highlight.

According to Zhao et al. (2016) and Silva et al. (2021), the parameter k concerns the inclination trend of the methane generation steps, i.e., a more accelerated degradation behavior, lower anaerobic digester volume, and shorter hydraulic detention time.

Table 3. Kinetic and statistical parameters of the 5 kinetic models studied for each configuration.

C	Model	y_m ($NmL.g^{-1}$ VS)	k (d^{-1})	μ ($NmL.d^{-1}$)	λ (d)	RSS ($NmL.g^{-1}$ VS)	R^2
DW	First Order	3.39E+04	9.97E-05	–	–	22940	0.961
	Modified Logistic	124.50	–	5.376	7.733	714.7	0.988
	Modified Gompertz	144.50	–	2.599	6.409	321.8	0.994
	Cone	189.40	0.037	–	–	233.6	0.996
	Fitzhugh	6.00E+05	5.86E-06	–	–	2285.0	0.960
DWb	First Order	180.80	0.025	–	–	2882.0	0.935
	Modified Logistic	92.32	–	7.178	6.050	226.3	0.995
	Modified Gompertz	95.14	–	2.954	5.532	99.3	0.998
	Cone	98.11	0.080	–	–	81.5	0.998
	Fitzhugh	180.60	0.161	–	–	2882.0	0.933

Legend: DW: Dog waste without bicarbonate; DWb: Dog waste with bicarbonate; y (t): Methane cumulative production ($NmL.g^{-1}$ VS); t: Experimental execution time (d); k: Hydrolysis constant (d^{-1}); : Methane maximum production ($NmL.g^{-1}$ VS); : Maximum methane production rate ($NmL.d^{-1}$); : Lag phase (d); n: Shape constant (dimensionless); RSS: Residual sum of squares; R^2: Determining factor.

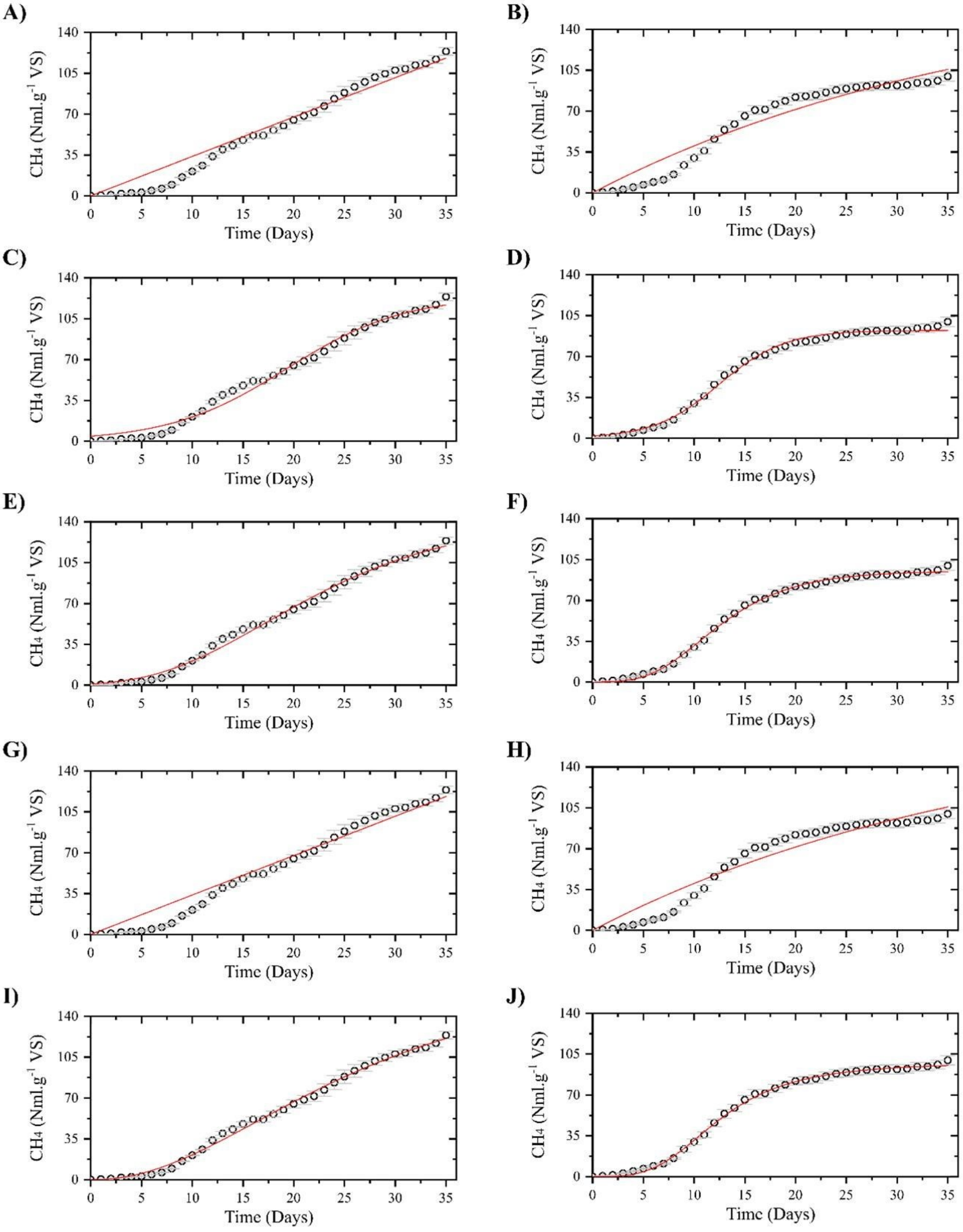
The maximum rate of methane production (μ) is equal to 5.376 $NmL.d^{-1}$ and 2.599 $NmL.d^{-1}$ for DW and 7.178 $NmL.d^{-1}$ and 2.954 $NmL.d^{-1}$ for DWb, both for the Gompertz model and modified Logistic, respectively, being DW presenting the maximum methane production rate (μ) superior.

The value of λ was equivalent to 7.733 d and 6.409 d for DW as well as 6.050 d and 5.532 d for DWb, both configurations in the sense of modified Logistic and modified Gompertz model. The DWb configuration presented a lower λ value, indicating that this sample has obtained a faster onset of methane generation.

It can be emphasized that all kinetic parameters used for this type of waste presented a great adjustment in the results, obtaining R^2 with values close to 1.

Being the best fit values for the Cone Model and Gompertz Model for the DW and DWb configurations, respectively, evidencing that, probably, the Cone Model serves for both configurations. Analyzing the Gompertz Model is perfectly adequate; being less complex, which favors simulation stages and scale-up of future projects.

Figure 5. The behavior of the evaluated kinetic models concerning the experimental data obtained for the configurations studied.



Legend: (A) - DW + 1st order kinetics; (B) - DWb + 1st order kinetics; (C) - DW + Logistic; (D) - DWb + Logistic; (E) - DW + Modified Gompertz; (F) - DWb + Modified Gompertz; (G) - DW + Fitzhugh; (H) - DWb + Fitzhugh; (I) - DW + Cone; (J) - DW + Cone.

Conclusion

Dog waste can be used as an excellent substrate for the anaerobic digestion process. The biogas generation potential (124 NmL.g^{-1}.VS) was similar animal waste which also presents high quality biogas in terms of methane concentration (~78% in CH_4).

The insertion of sodium bicarbonate as an alkalizing agent did not favor a faster stabilization of the residue, nor an increase in the methane potential and in the quality of the biogas in terms of methane concentration. The sodium concentration in bicarbonate may have negatively influenced the bacteriostatic effect, affecting more sensitive organisms in AD. This fact becomes an advantage, as there is no additional cost with alkalizing. The five kinetic models used were compatible with the experimental data and showed excellent fits, but the Cone model showed the best fit for both study configurations. It is also understood that this alternative can be interesting to reduce the dispersion of zoonotic diseases due to its intrinsic relationship with the dispersion of these residues in urban areas.

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