


Environmental Technology


Correlations between biogas and dissolved methane generated and physical-chemical parameters of sewage in modified full-scale UASB-type reactors

Correlações entre biogás e metano dissolvido gerados e parâmetros físico-químicos do esgoto em reatores tipo UASB modificado em escala real

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ABSTRACT

Anaerobic technology is widely used in Brazil for the treatment of domestic sewage, due to favorable conditions such as a hot climate and lower operational costs. In this process, by-products such as biogas are formed, which can be recovered and converted into energy. Accordingly, the present study aimed to report the correlations between biogas production—both in gaseous and dissolved forms—and domestic sewage parameters, using full-scale modified UASB-type reactors installed in Curitiba, Paraná. Measurements were performed in real time over five months. The monitored influent and effluent parameters included pH, temperature, alkalinity, acidity, TSS, VSS, FSS, COD, sulfate, dissolved methane, and flow rate. Biogas parameters included flow rate and the concentrations of methane, carbon dioxide, and hydrogen sulfide. To assess the relationships between variables in the gaseous and liquid phases, Spearman's correlation tests were applied. Operational results showed low removal efficiencies for BOD, COD, and TSS, attributed to the open design of the three-phase separator in this type of reactor. Most of the correlations between influent and effluent sewage parameters and biogas flow were moderate and positive, indicating that as biogas flow increased or decreased, these parameters tended to follow the same trend. However, correlations between sewage parameters and dissolved methane concentrations were weak or statistically non-significant, suggesting the need for further studies to better understand the influencing factors behind this relevant but often overlooked methane fraction.

Keywords: Biogas; Dissolved methane; Sewage; Statistical correlations; UASB reactors

RESUMO

A tecnologia anaeróbia é amplamente utilizada no Brasil para o tratamento de esgoto doméstico, devido a condições favoráveis, como clima quente e menores custos operacionais. Nesse processo, subprodutos como o biogás são formados, os quais podem ser recuperados e convertidos em energia. Nesse contexto, o presente estudo teve como objetivo relatar as correlações entre a produção de biogás — nas formas gasosa e dissolvida — e os parâmetros do esgoto doméstico, utilizando reatores anaeróbios do tipo UASB modificado em escala real, instalados em Curitiba – Paraná. As medições foram realizadas em tempo real, ao longo de cinco meses. Os parâmetros monitorados no afluente e no efluente incluíram pH, temperatura, alcalinidade, acidez, SST, SSV, SSF, DQO, sulfato, metano dissolvido e vazão. Os parâmetros do biogás incluíram vazão e concentrações de metano, dióxido de carbono e sulfeto de hidrogênio. Para avaliar as relações entre as variáveis nas fases gasosa e líquida, foram aplicados testes de correlação de Spearman. Os resultados operacionais demonstraram baixas eficiências de remoção de DBO, DQO e SST, atribuídas ao desenho aberto do separador trifásico desse tipo de reator. A maioria das correlações entre os parâmetros do esgoto (afluente e efluente) e a vazão de biogás foram moderadas e positivas, indicando que, à medida que a vazão de biogás aumentava ou diminuía, esses parâmetros seguiam a mesma tendência. No entanto, as correlações entre os parâmetros do esgoto e as concentrações de metano dissolvido foram fracas ou estatisticamente não significativas, sugerindo a necessidade de novos estudos para melhor compreender os fatores que influenciam essa fração relevante, porém frequentemente negligenciada, do metano.

Palavras-chave: Biogás; Metano dissolvido; Esgoto doméstico; Correlações estatísticas; Reatores UASB

1 INTRODUCTION

Anaerobic digestion (AD) is a natural process in which a consortium of microorganisms, working in syntrophy, converts carbonaceous organic matter into energy, producing biogas as a by-product. This gas has in its composition methane, carbon dioxide, hydrogen and hydrogen sulfide, whose compositions vary according to the degraded substrate (Angelidaki, Batstone, 2011), because it is flammable, biogas can be used as a source of energy, both electrical, through conversions in engines, and thermal, through its burning (Rafie *et al.*, 2020).

Despite its robustness, the AD process is influenced by some operational parameters. For example, the organic loading rate, pH, temperature, and hydraulic retention time, among others, can be mentioned. In addition to the influence of design conditions, it is necessary to have a system with a large mass of bacteria and to maintain sufficient contact between the organic material in the sewage and the mass of microorganisms (Li, Hen, Wu, 2019).

The first time that anaerobic technology was used intentionally for wastewater treatment was in 1881, by Mouras in France, in an early version of the septic tank (Abbasi, Tauseef, Abbasi, 2011). In the following century, several reactors were developed, aiming to improve their efficiency and operational parameters. One notable example is the UASB-type reactor, developed by Lettinga in the early 70s. In this type of upflow reactor, the biomass remains suspended at the bottom of the reactor (sludge blanket), while a compartment at its top, called a three-phase separator (3PHS), collects the generated biogas (Lettinga *et al.*, 1980, Seghezze *et al.*, 1998).

Due to the required temperatures, operational ease, and lower associated costs (compared to aerobic technologies), this process was widely adopted in hot-climate developing countries, such as Brazil, India, Mexico, and Colombia, among others (Chernicharo, 2006). A study carried out in 2016 for Brazil showed that 72% of the country's sewage treatment plants used at least one anaerobic process, and 38% employed a UASB-type reactor (Von Sperling, 2016).

The gases generated in these anaerobic reactors, to varying degrees, are solubilized in the liquid, which makes it difficult to capture them normally and to direct them to the appropriate destination (Souza, Chernicharo, Melo, 2012). The methane dissolved in the effluent, for example, is often not recovered and ends up escaping into the atmosphere, contributing to the greenhouse effect. Moreover, since it has energy potential, such a loss can be considered a waste of resources. Henry's law defines the amount of gas that can be solubilized in a given liquid as a function of the associated temperature and pressure. However, experimental studies demonstrate concentrations that differ from those predicted by the aforementioned law, generally higher than they should be, indicating methane supersaturation in the liquid. These differences can lead to erroneous estimates regarding the total amount of biogas produced in the treatment plants (Crone *et al.*, 2016, Centeno-Mora *et al.*, 2020, Ramos *et al.*, 2021).

According to Cookney *et al.* (2012), in UASB reactors, the inefficient hydraulic mixing and low flow velocities make it difficult for the dissolved gas to reach the three-

phase separator, contributing to the supersaturation of methane in the effluent. Similarly, Matsunaga *et al.* (2012) suggest that the carriage of solids and biomass, potentially with adhered biogas, also contributes to the gas's supersaturation.

In light of the importance of understanding the factors that influence biogas yield in anaerobic systems—especially the fraction dissolved in the effluent—this study aimed to report the results of correlations between biogas production and domestic sewage parameters in full-scale modified UASB-type reactors.

2 MATERIALS AND METHODS

The operation of the modified UASB-type reactor was monitored to verify its performance, particularly in terms of the removal of carbonaceous organic matter and the production of biogas. The following sections present the methodology employed in the research.

2.1 Study Area

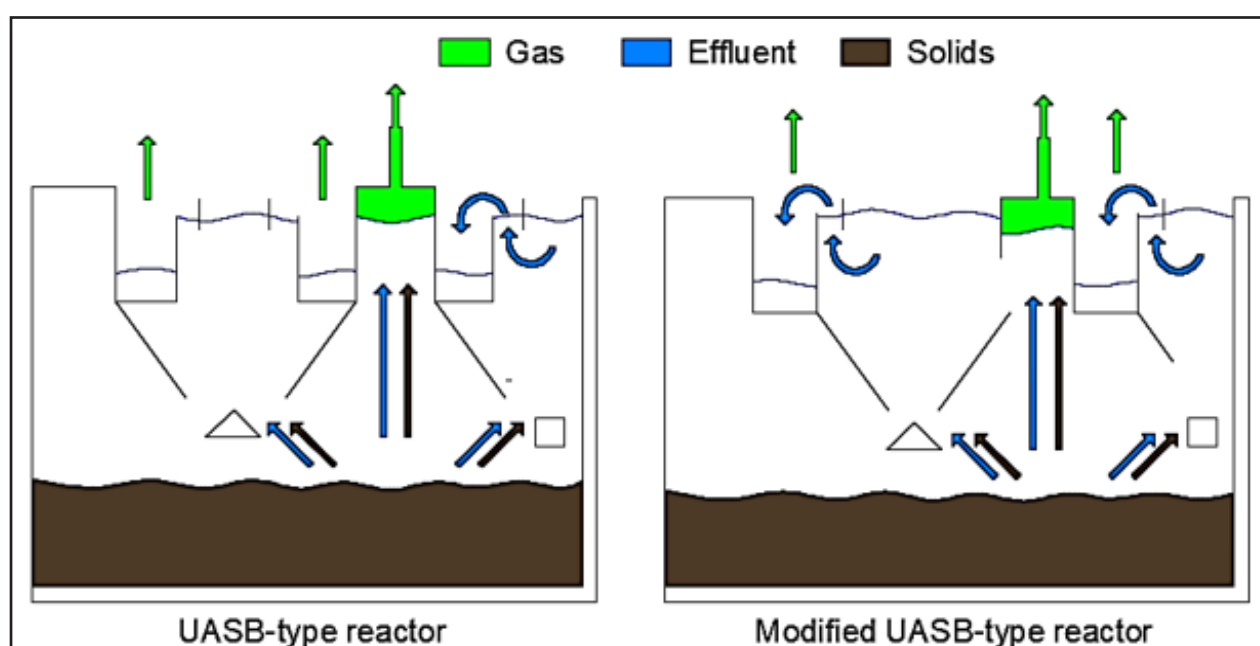
The experiments were carried out in a full-scale WWTP, located at coordinates 25°33'39" S and 49°14'44" O, in Curitiba - Paraná. The WWTP has been operating since 2002 and was designed to treat 440 L s⁻¹. During the study period, the WWTP served a population of approximately 252,764 inhabitants and had an average inflow of 340 L s⁻¹, ranging from 84 to 604 L s⁻¹.

The treatment system consisted of preliminary treatment, biological treatment (consisting of six modified UASB-type reactors), and post-treatment, including a mixed aerated lagoon and a sedimentation lagoon.

Each modified UASB-type reactor had a nominal flow capacity of 70 L s⁻¹, volumetric capacity of approximately 2,000 m³, and hydraulic retention time (HRT) of approximately 8 hours. The particularity of these reactors compared to traditional UASB-type reactors is the increased spacing between the three-phase separator (3PHS) and the settling area, which allows the discharge of finer floated sludge flakes (Ross, 2015).

This design aims to reduce the accumulation of scum within the separator, facilitating its removal and maintaining the hydraulic flow. However, this configuration involves a design trade-off: while it helps prevent blockages and improves flow dynamics, it may also permit greater solids carryover with the effluent due to the wider opening at the top. Figure 1 illustrates the difference between the two reactor configurations.

Figure 1 – Schematic representation of a traditional UASB-type reactor and a modified UASB-type reactor



Source: Authors (2023)

Biogas generated during the treatment of sewage at the WWTP was sent to enclosed flares, where partial methane destruction occurred, with an efficiency greater than 99%. Moreover, the sludge generated was sent to a decanter-type centrifuge and dewatering system, underwent sanitization (pathogen reduction), and finally, was sent for agricultural use.

2.2 Sampling and analysis of sewage and biogas

The performance of the modified UASB-type reactors was evaluated through the analysis of influent and effluent samples collected by two automatic samplers

(Teledyne ISCO® 3700 and Hach® Sigma SD900), both installed in the WWTP. These devices were programmed to collect 1,000 mL samples every hour, for three consecutive days in a week (Monday, Tuesday, and Wednesday). Samples were taken from the collectors after the one-day collection period (24 samples). This procedure was repeated over five months (July to November), covering both winter and spring in the Southern Hemisphere. Moreover, given that some analyses have peculiarities, such as the need for immediate execution or the use of preservatives, and therefore cannot be performed with samples obtained by automatic collectors, grab samples were also collected. These grab samples were taken from the same locations where the automatic samplers were installed.

The following parameters were determined according to procedures described in APHA (2017): pH (4500H⁺), biochemical oxygen demand (BOD) (5210B), total alkalinity (2320), acidity (2310), TSS (2540), VSS (2540), and FSS (2540). Temperature was measured with a thermometer, chemical oxygen demand (COD) was measured by the Hach 8000 reactor digestion method, adapted from Jirka and Carter (1975), and sulfate was measured by the Hach 8051 - SulfaVer 4 method, adapted from APHA (2017). The sewage flow rate was obtained through the ultrasonic flow meter coupled with a Parshall flume at the WWTP sewage inlet. Influent and effluent pH, temperature, BOD, and sulfate, as well as influent alkalinity and acidity, were analyzed three times a day using grab samples. The other parameters were analyzed 24 times a day using samples collected by the automatic samplers, totaling 4,320 data points.

Biogas production (flow rate) was monitored by a thermal dispersion flow meter (Thermathel® TA2 Enhanced, Magnetrol), with a measuring range from 0.05 Nm³ s⁻¹ to 200.00 Nm³ s⁻¹ and a resolution of ± 1%. This device consists of a transmitter and probe with temperature sensors. The device provided normalized biogas flow measurements. For data storage, the meter was connected to a data logger, configured to record the flow rate every 30 seconds. As measurements were taken over three consecutive days, repeated over the five months, 34,560 data points were collected for the biogas flow.

The methane, carbon dioxide, and hydrogen sulfide concentrations in the biogas were obtained by a fixed gas meter (BioControl, Multitec® 545, Sewerin). This gas meter is a gas analyzer that uses an infrared sensor to determine CH₄ concentration and electrochemical sensors to measure CO₂ and H₂S concentrations. The results were transmitted every 5 minutes to an online platform, totaling 12,960 data points. Ramos *et al.* (2021), Duarte Hernandez *et al.* (2021), and Michelin *et al.* (2022) also used infrared sensors to determine CH₄ in the biogas generated from anaerobic reactors treating sewage.

The concentration of methane dissolved in the effluent was measured according to the method described by Souza *et al.* (2011). The theoretical methane saturation in the liquid phase at the equilibrium was obtained using Henry's law, as shown in Equation (1).

$$[CH_4]_{eq} = k_H * P_{gas} \quad (1)$$

Where:

[CH₄]_{eq} is the concentration of dissolved methane in equilibrium (mg L⁻¹);

k_H is the Henry's Law constant (mg L⁻¹ atm⁻¹);

P_{gas} is the gas partial pressure (atm).

The degree of dissolved methane saturation was obtained as the ratio between the experimentally measured concentration and the theoretical concentration (Equation 2).

$$S.D. = \frac{[CH_4]_{dis}}{[CH_4]_{eq}} \quad (2)$$

Where:

S.D. is the degree of dissolved methane saturation (dimensionless);

[CH₄]_{dis} is the concentration of dissolved methane (mg L⁻¹);

[CH₄]_{eq} is the concentration of dissolved methane in equilibrium (mg L⁻¹).

2.3 Statistical analysis

Statistical analyses were performed using Minitab® 18 software. Since most of the data were not normally distributed, Spearman's rank correlation coefficients (ρ) were calculated between biogas flow and the parameters: sewage flow rate, influent COD, alkalinity, TSS, VSS, FSS and temperature; as well as between the concentration of methane dissolved in the effluent and sewage flow rate, influent and effluent TSS, temperature and methane concentration in biogas.

According to Xiao *et al.* (2016), the Spearman rank correlation coefficient is a non-parametric or distribution-free rank statistical measure of the strength and the direction of the arbitrary monotonic association between two ranked variables or one ranked variable and one measurement variable. Its value ranges from -1.0 to 1.0. Positive values denote positive correlations, while negative values denote negative ones; zero denotes no correlation. McSeveny *et al.* (2009) denoted the following five strength levels for ρ : a) very weak: 0 to 0.19; b) weak: 0.20 to 0.39; c) moderate: 0.40 to 0.59; d) strong: 0.60 to 0.79; e) very strong: 0.8 to 1.0.

3 RESULTS AND DISCUSSION

3.1 Performance of the modified UASB-type reactor

Figures 2a to 2f show the values of pH, temperature, total alkalinity, acidity, BOD, COD, TSS, and VSS in the influent and effluent throughout the reactor monitoring period.

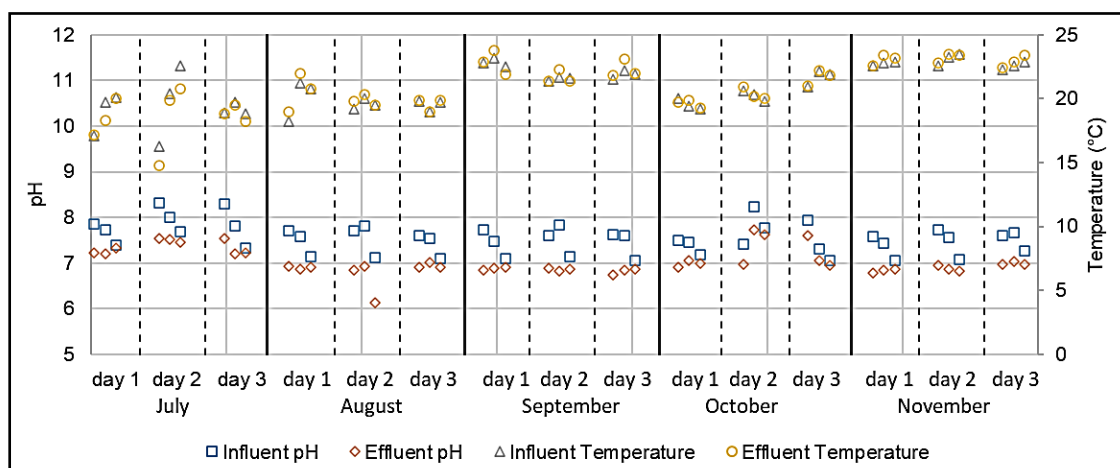
Depending on the temperature at which it occurs, anaerobic digestion can be psychrophilic ($< 20\text{ }^{\circ}\text{C}$), mesophilic ($20\text{--}45\text{ }^{\circ}\text{C}$), or thermophilic ($45\text{--}60\text{ }^{\circ}\text{C}$), with anaerobic digesters usually operated in these last two ranges (Safley Jr and Westerman, 1992, Suryawanshi, Chaudhari, Kothari, 2010). The operational temperature ranged from 16.3 to 23.5°C , with an average of $20.9 \pm 1.7^{\circ}\text{C}$. The reactor operated in the psychrophilic range for approximately one-third of the time, and in the mesophilic range for the

remainder. The lower temperatures observed during the first two months can be attributed to winter conditions in the study region.

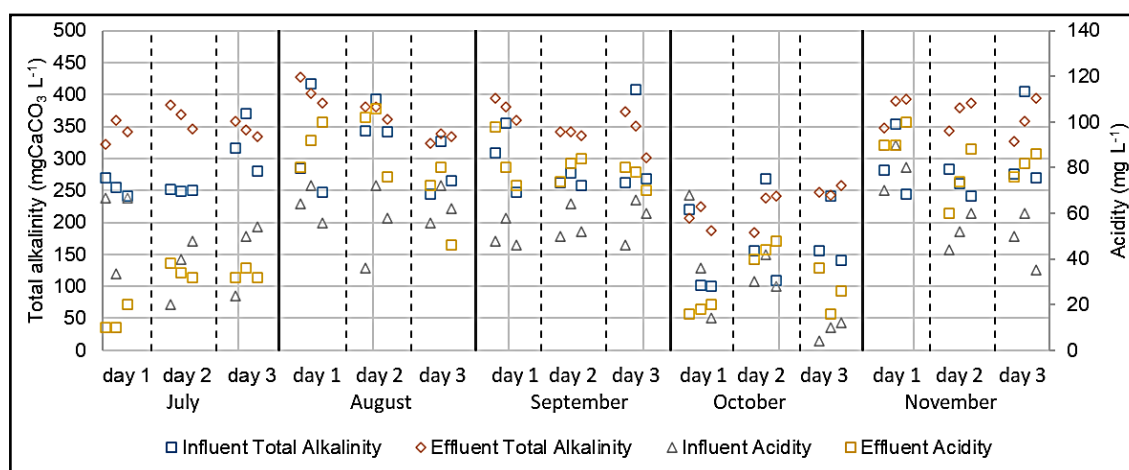
Figure 2 – Influent and effluent pH and temperature (a); alkalinity and acidity (b); BOD (c); COD (d); TSS (e); and VSS (f) measured over the monitoring period

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(a)

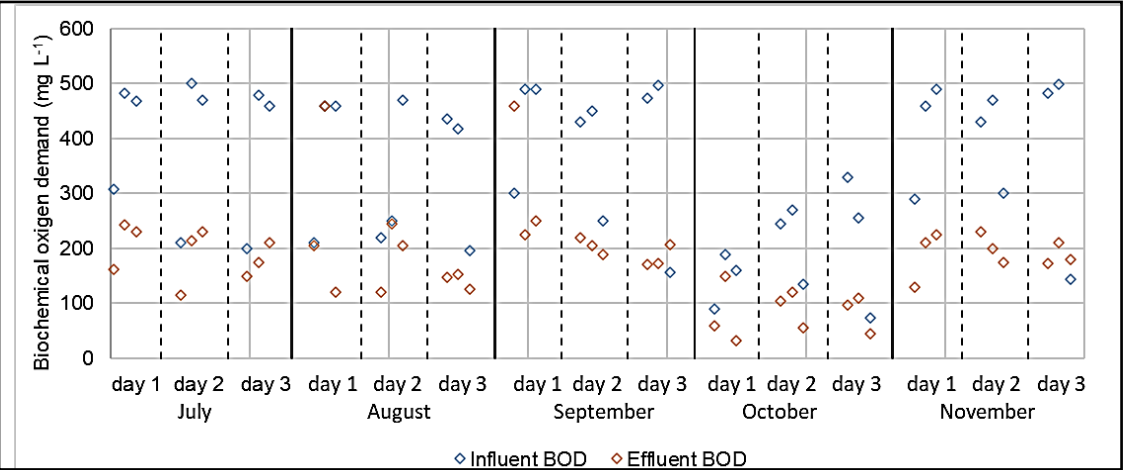


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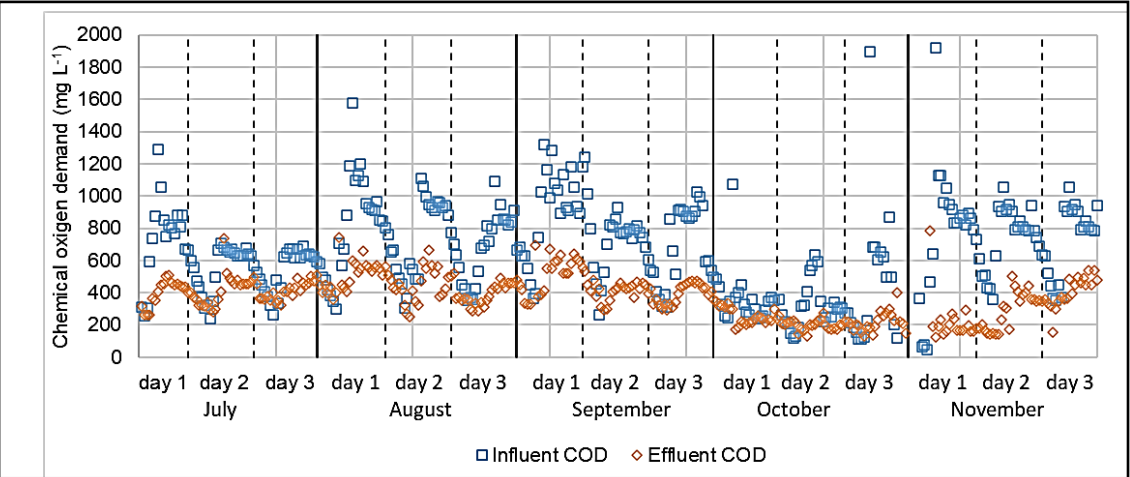


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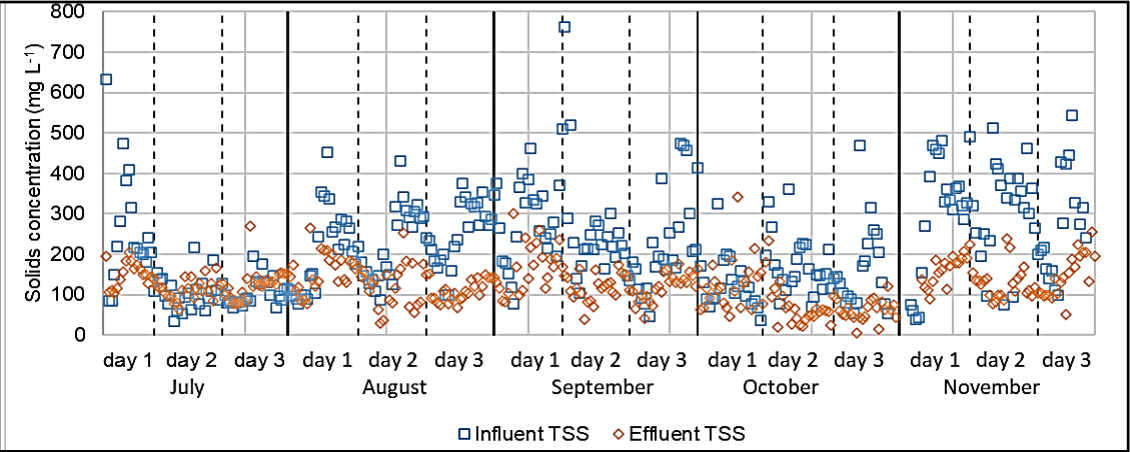
c)



d)

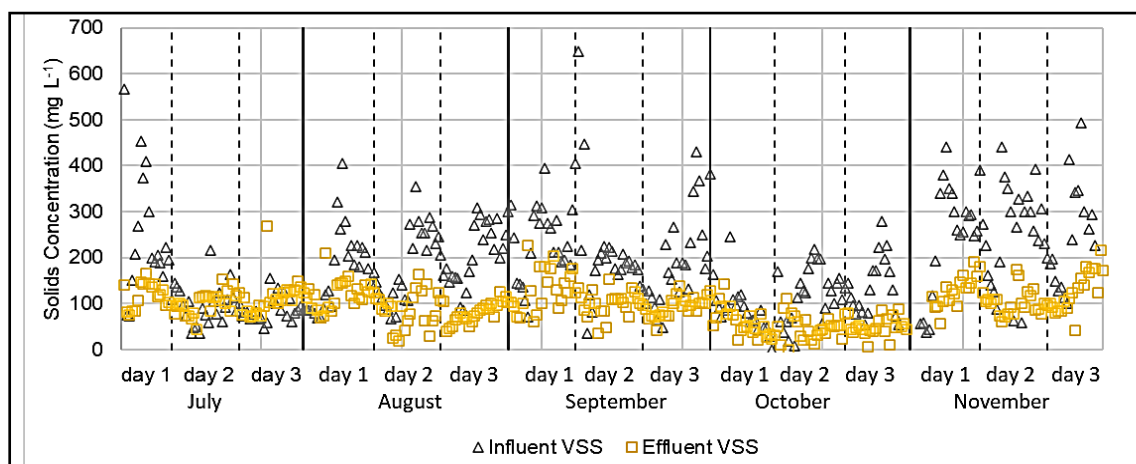


e)



(Conclusion)

f)



Source: Authors (2023)

The average influent pH was 7.6 ± 0.3 , while the average effluent pH was 7.0 ± 0.3 during operation. Although a decrease was observed, the effluent value can still be considered suitable for the development of methanogenic archaea, which require a pH between 6.5 and 7.5 (LI and WU, 2019). The average total alkalinity in the effluent samples was $324 \pm 62 \text{ mgCaCO}_3 \text{ L}^{-1}$, with an average increase of 31% compared to the influent concentration of $269 \pm 76 \text{ mgCaCO}_3 \text{ L}^{-1}$. The average acidity in the effluent was $62 \pm 29 \text{ mg L}^{-1}$, a slight increase compared to $49 \pm 20 \text{ mg L}^{-1}$ in the influent. This may help explain the previously mentioned reduction in pH. The increase in TA and the relatively low acidity in the effluent indicate the buffering capacity of the modified UASB-type reactor, demonstrating the neutralization of volatile acids.

The average influent BOD was $346 \pm 137 \text{ mg L}^{-1}$, while the average influent COD was $650 \pm 292 \text{ mg L}^{-1}$. Due to the 24 daily COD measurements, cyclical variations were observed, with a period of approximately 24 hours. The average daily COD variation amplitude was $805 \pm 388 \text{ mg L}^{-1}$. These variations explain the high standard deviation (45% of the mean) and were likely related to daily patterns in population activity, as stated by Metcalf and Eddy (1980). i.e., for a given population, sewage flow rate and composition typically vary over a day, with higher organic loads during periods of

increased water use, such as mornings and evenings. In contrast, the average effluent COD was $370 \pm 129 \text{ mg L}^{-1}$, with an average daily amplitude of $294 \pm 193 \text{ mg L}^{-1}$. Since effluent COD showed lower variations compared to the influent, it can be inferred that the reactor effectively absorbed fluctuations in organic loading without compromising process stability. The average effluent BOD concentration was $180 \pm 83 \text{ mg L}^{-1}$.

The average BOD and COD removal efficiencies were 43 ± 28 and $34 \pm 32\%$, respectively. Since the COD fraction includes non-biodegradable material, higher BOD removal was expected. COD removal was significantly lower than the range of 65–85% reported by Khan *et al.* (2015), the 65% found by Santos *et al.* (2018), and the 45 - 86% noted by Kalash *et al.* (2021) for traditional UASB-type reactors treating sewage. One possible explanation is that the wider opening in the three-phase separator (3PHS) of the modified UASB reactor allowed more solids to escape with the effluent, promoting organic matter washout. In several COD and BOD evaluations, higher concentrations were found in the effluent than in the influent. Despite the lower efficiencies, the WWTP still complies with Brazilian regulations due to post-treatment through a mixed aerated lagoon and a sedimentation lagoon, which are not the focus of this paper. However, lower BOD removal implies that a significant amount of organic matter remains in the effluent, potentially overloading subsequent treatment stages and likely increasing operational costs.

Regarding TSS, concentrations behaved similarly to COD: cyclical in the influent, with a roughly daily pattern, and more stable in the effluent. The average influent and effluent concentrations were $227 \pm 196 \text{ mg L}^{-1}$ and $126 \pm 53 \text{ mg L}^{-1}$, respectively. The average removal efficiency was $26 \pm 54\%$, lower than the $54 \pm 16\%$ reported by Khan *et al.* (2015) and the 65–90% indicated by Crone *et al.* (2016) for UASB-type reactors. This reduced efficiency may be attributed to operational control routines and the current state of the infrastructure. Van Lier *et al.* (2010) reported that many newly built UASB reactors do not achieve satisfactory performance due to inadequate operation and insufficient monitoring. It should also be noted that

efforts were made to maintain the sludge blanket height within the operational limits recommended by the sanitation company. Finally, as with COD and BOD, the structural differences between the modified UASB and traditional configurations may partially account for the lower efficiency.

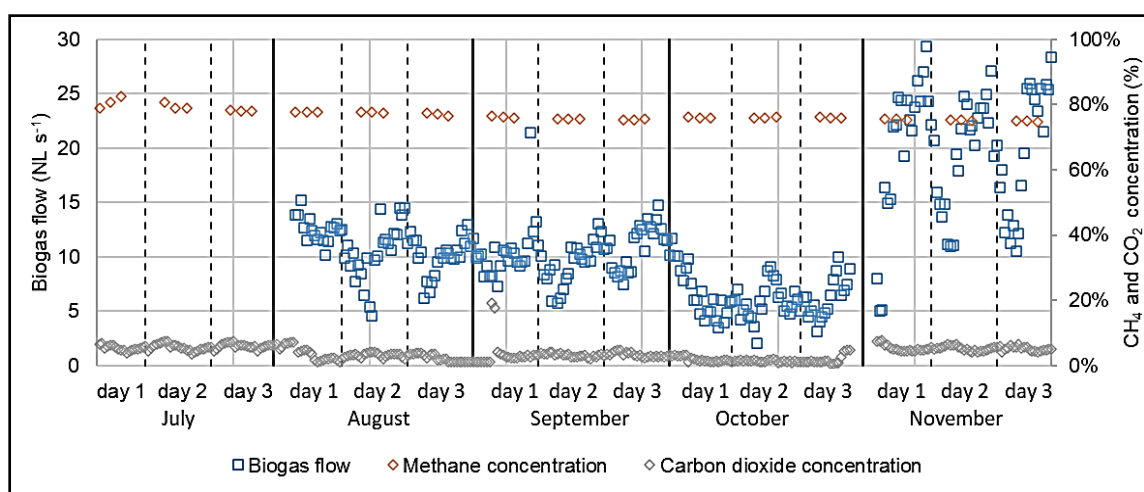
3.2 Biogas yield and concentrations of gases in the reactor

Figures 3a to 3c present the profiles of biogas flow, concentrations of CH_4 , CO_2 , and H_2S in the biogas, experimentally and theoretically obtained methane dissolved in the effluent, and the calculated saturation degree of this gas.

Figure 3 – Biogas flow and concentrations of CH_4 and CO_2 (a); influent and effluent sulfate and concentration of H_2S (b); and measured dissolved methane, theoretical dissolved methane, and saturation degree (c) over time.

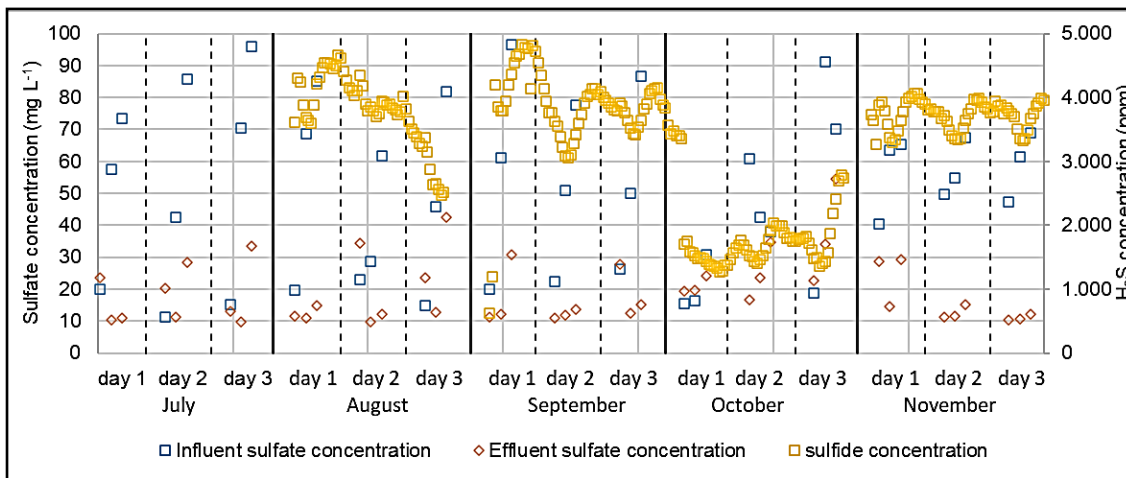
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(a)

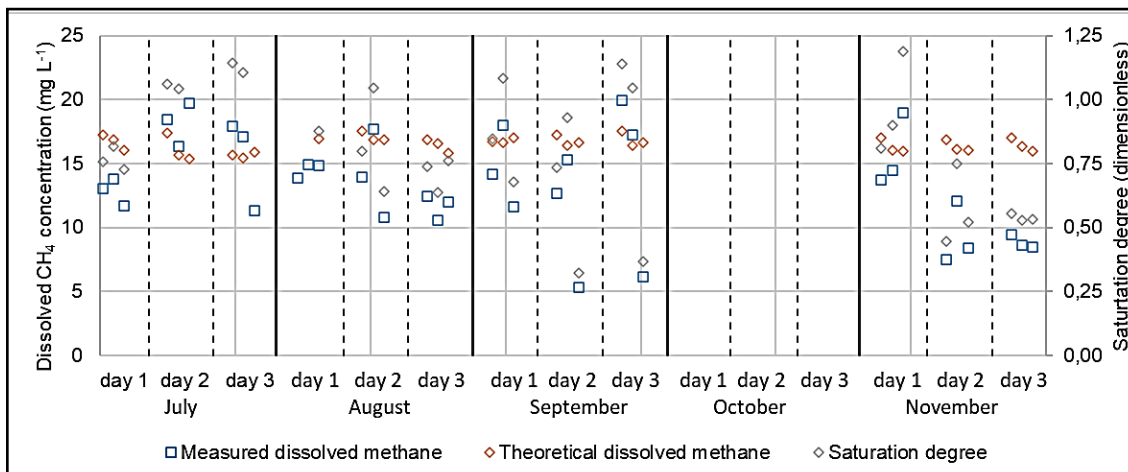


(Conclusion)

(b)



(c)



Source: Authors (2023)

The average biogas production in the modified UASB-type reactor was $12.05 \pm 6.17 \text{ N L s}^{-1}$, ranging from 2.07 N L s^{-1} to 29.33 N L s^{-1} . In general, it can be observed that the biogas flow exhibited standard curves with a period of approximately one day, showing alternating maximum and minimum flows and a variable, periodic, and non-stationary temporal behavior, as described by Possetti *et al.* (2013), Duarte Hernandez *et al.* (2018), and Paula *et al.* (2018).

By considering an expected 0.075 L of biogas per liter of sewage, the average expected biogas production should be approximately 25 L s^{-1} . It is possible that this

type of modified reactor loses a significant amount of biogas through the openings in the three-phase separator, along with TSS.

The maximum biogas production at the treatment plant usually occurred at two times during the day: between 7 and 8 a.m. and between 11 p.m. and 12 a.m., possibly due to variations in organic matter concentration throughout the day. Possetti *et al.* (2013) showed that the maximum biogas production flow generally occurs between 12 and 2 a.m. This behavior differs from the pattern observed in the present study. According to Duarte Hernandez *et al.* (2018), several factors may explain differences in peak times across different plants, including the shape of the watershed contributing to the plant, the habits and socio-economic status of the local population, the configuration and structure of pipelines and networks, the presence of industrial wastewater, among others.

Regarding biogas composition, the average CH₄ concentration in the biogas generated in the reactor was $81 \pm 0.04\%$. Louros *et al.* (2021) also reported 81% CH₄ in the biogas from a UASB-type reactor treating synthetic wastewater. The concentration observed in the present study was slightly higher than the 60–75% and $67 \pm 8\%$ reported by Souza *et al.* (2011) and Owusu-Agyeman *et al.* (2021), respectively, for UASB-type reactors treating sewage.

The average CO₂ concentration was $4 \pm 2\%$, which falls within the 0.7–6.2% range reported by Duarte Hernandez *et al.* (2021), and is higher than the $2.3\text{--}2.7 \pm 0.5\%$ reported by Owusu-Agyeman *et al.* (2021). Finally, the average H₂S concentration was $3,421 \pm 1,072$ ppm, slightly above the 2,000 ppm found by Owusu-Agyeman *et al.* (2021) and the 1,200–2,000 ppm reported by Souza *et al.* (2012).

It was observed that sulfate reduction by sulfate-reducing bacteria (SRB) occurred, with an average removal efficiency of $46.5 \pm 44\%$. It should be noted that in 18% of the samples, effluent sulfate concentrations were higher than influent values, thereby lowering the average and increasing the standard deviation. The activity of SRB is evident, as a reduction in average sulfate concentration was

observed from $51.01 \pm 25.31 \text{ mg L}^{-1}$ in the influent to $19.41 \pm 10.27 \text{ mg L}^{-1}$ in the effluent. The reduction of sulfate to sulfide also results in the formation of hydrogen sulfide (H_2S) within the reactor, which is considered one of the main odorant gases in WWTPs and is flammable, corrosive, and toxic. This occurs because sulfides, when present in the liquid phase, are easily released into the atmosphere in gaseous form (Chen *et al.*, 2011, Zhang *et al.*, 2013).

The average concentration of methane dissolved in the effluent of the reactor was $13.40 \pm 3.85 \text{ mg L}^{-1}$, ranging from 5.32 mg L^{-1} to 19.95 mg L^{-1} . These values were similar to the $12.5 \pm 3.5 \text{ mg L}^{-1}$ reported by Huete *et al.* (2018) at 19.7°C ; the 8.5 mg L^{-1} verified by Nelting *et al.* (2015) at $20\text{--}25^\circ\text{C}$; the 10 mg L^{-1} to 14.6 mg L^{-1} noted by Ramos *et al.* (2021) at $18\text{--}28^\circ\text{C}$; the 17 to 22 mg L^{-1} obtained by Souza *et al.* (2011) at 25°C ; and the 14.9 mg L^{-1} found by Santos *et al.* (2022) at 29.9°C .

The average percentage loss of dissolved methane in the effluent from the modified UASB-type reactor was 43%, similar to the 45% reported by Cookney *et al.* (2012) at 25°C , 39% by Souza *et al.* (2011) at 24°C , and 38% by Ramos *et al.* (2021) at 28°C . Also, the value found in the present study is consistent with the range estimated by Chernicharo *et al.* (2015), who reported methane losses between 36 and 40% in the effluent of anaerobic reactors operating in Brazil.

The theoretical concentrations of dissolved methane, calculated using Henry's Law, showed little variation, resulting in fluctuations in the saturation degree corresponding to each concentration. These generally followed the trend of the experimentally measured values, with an average of 0.81 ± 0.25 , ranging from 0.32 to 1.28. When the degree of saturation was 0.32, the experimental concentration was approximately 30% of the expected by Henry's Law; conversely, when the degree was 1.28, the experimental concentration was about 30% higher than the theoretical value. These values are within the range of 0.32 to 6.90 reported by Nelting *et al.* (2015), Yeo and Lee (2013), Crone *et al.* (2016), Ramos *et al.* (2021), and Santos *et al.* (2022) for different anaerobic reactors operated between 6 and 31°C .

3.3 Correlation between parameters

Table 1 presents the Spearman correlation coefficients between the physicochemical parameters of the influent and both the biogas flow and the dissolved methane concentration.

Table 1 – Spearman correlation coefficient between the physicochemical parameters of the influent and the biogas flow and dissolved methane concentration

Parameters	Biogas Flow		Dissolved methane	
	Spearman's ρ	p-value	Spearman's ρ	p-value
Sewage flow rate	-0.29a	0.000	-0.09b	0.5896
Influent COD	0.59a	0.000	-	-
Influent ALK	0.45a	0.006	-	-
Influent TSS	0.58a	0.000	-0.21b	0.2278
Effluent TSS	-	-	-0.08b	0.6479
Influent VSS	0.62a	0.000	-	-
Influent FSS	0.30a	0.000	-	-
Temperature	0.53a	0.001	-0.11b	0.5288
Methane concentration in biogas	-	-	-0.14b	0.4339

Source: Authors (2023)

Note: ^aStatistically significant correlation (p-value < 0.05). ^bNon-statistically significant correlation (p-value > 0.05)

Spearman's ρ between sewage flow rate and biogas flow was -0.29, indicating a weak and inversely proportional correlation, as reported by Cabral (2016). This behavior may be attributed to dilution effects—where increased flow rates lower the concentration of organic matter—and to the reduction in hydraulic retention time (HRT), which decreases the contact time between microorganisms and substrate, potentially limiting methane production. Both factors can influence the activity of

methanogenic archaea, thereby affecting biogas yield. The Spearman correlation coefficient between influent COD and biogas production was 0.59, indicating a moderate positive correlation between the incoming organic material and biogas yield. This suggests that when the concentration of available organic matter increased, microorganisms were able to convert more of it into biogas, with gas production following this trend—as also observed by Duarte Hernandez et al. (2018), Duarte Hernandez *et al.* (2021), and Michelin *et al.* (2022).

Regarding influent alkalinity, Spearman's ρ between this parameter and biogas production was 0.45, indicating a moderate positive correlation. i.e., when influent sewage alkalinity increased or decreased, biogas flow also increased or decreased accordingly. Since alkalinity functions as a buffer during the sewage treatment process, it helps prevent sudden changes in pH, thereby favoring the activity of methanogenic archaea (McCarty, 1974). Thus, the positive correlation observed between sewage alkalinity and biogas production is justified.

The concentration of solids in the influent showed a positive correlation with biogas production. The strength of the correlation varied, being moderate for TSS, strong for VSS, and weak to very weak for FSS. As VSS represents the organic fraction present in sewage, its higher presence indicates more available substrate for the microorganisms responsible for organic matter degradation. Therefore, the greater the availability of substrate for methanogenic archaea, the greater the biogas production and release—similar to what was observed for COD. Conversely, FSS represents the inert fraction of domestic sewage and is not utilized during anaerobic digestion. This explains the weak to very weak correlations observed for this parameter. Additionally, TSS represents the sum of both organic and inert fractions, justifying the moderate correlation observed between TSS and biogas production (Paula, 2019).

The Spearman correlation coefficient (ρ) between temperature and biogas production in the modified UASB-type reactor was 0.53, indicating a moderate positive correlation. Ramos *et al.* (2021) reported a Pearson correlation coefficient of

0.57 between methane collected from an Upflow Anaerobic Hybrid (UAHB) reactor and temperature—thus, a similar magnitude to the correlation found in this study. According to Lettinga *et al.* (1993), temperature is one of the most influential factors in the efficiency of anaerobic digestion, as it affects the growth rate and metabolism of microorganisms, ionic balance, and substrate solubility. These aspects help justify the positive correlation observed between temperature and biogas production.

Regarding the relationship between influent sewage flow rate and dissolved methane in the effluent, the Spearman coefficient (-0.09) indicated a very weak negative correlation. However, the p-value (0.5896) indicated a non-statistically significant correlation. Therefore, there is no evidence to support a meaningful relationship between influent sewage flow rate and dissolved methane concentration in the effluent based on the data analyzed. According to Souza *et al.* (2011) and Cookney *et al.* (2012), hydraulic mixing in UASB reactors is inefficient, which impairs methane migration to the reactor headspace. Thus, a significant correlation between dissolved methane and sewage flow rate was expected, due to its association with the hydraulic mixing condition and the biogas flow, both of which influence the internal dynamics of the reactor.

For the correlations between dissolved methane and temperature and methane concentration in the biogas, Spearman's coefficients were -0.11 and -0.14 , respectively, indicating very weak negative correlations. However, the corresponding p-values (0.5288 and 0.4339) were above the adopted significance level ($\alpha = 0.05$), indicating non-statistically significant correlations. Henry's Law defines the solubility of gases in liquids as a function of temperature and the partial pressure of the gas above the liquid surface, the latter being related to the gas concentration in the headspace (Atkins, Jones, Laverman, 2006)—in this case, the methane concentration in the biogas. Therefore, significant correlations were also expected for these parameters, which were not observed in this study. Furthermore, the lack of statistically significant correlations with Henry's Law parameters may explain the variations in the saturation degree observed. Ramos *et al.* (2021) reported a very strong negative correlation ($r = -0.86$) between temperature

and the concentration of dissolved methane in the effluent of a UASB reactor treating synthetic sewage; i.e., the higher the temperature, the lower the dissolved methane concentration. However, in their study, temperature remained stable within each operational phase, unlike the current study, where temperature varied continuously.

For influent TSS and dissolved methane, Spearman's coefficient was -0.21 , suggesting a weak negative correlation. The same coefficient for effluent TSS and dissolved methane was -0.08 , indicating a very weak negative correlation. Nevertheless, for both cases, the p-values (0.2278 and 0.6479) exceeded the 0.05 significance threshold, indicating non-significant correlations. According to Crone *et al.* (2016), biomass with adhered biogas can increase the concentration of dissolved methane in the effluent when carried out of the reactor. Therefore, significant correlations were expected, considering that influent TSS concentration was $227 \pm 196 \text{ mg L}^{-1}$, and effluent TSS concentration was $126 \pm 52 \text{ mg L}^{-1}$, indicating low removal efficiency and potential carryover of solids with biogas.

One hypothesis is that the openings in the three-phase separator of the modified UASB-type reactor may be contributing to the lower concentrations of dissolved methane. These openings may not only allow solids to escape, but also facilitate the release of biogas bubbles that may carry, aggregate, and strip dissolved methane, which then escapes into the atmosphere from the surface of the settling tank/reactor. Overall, the combination of physical, operational, and environmental factors—such as reactor configuration, limited mixing, temperature fluctuations, influent variability, and mass transfer limitations—may collectively contribute to the patterns observed in dissolved methane concentration.

4 CONCLUSIONS

Operationally, the full-scale modified UASB-type reactors maintained appropriate pH and temperature levels. The system's buffering capacity was also confirmed, based on ideal concentrations of alkalinity and acidity. However, the system's efficiency in removing BOD, COD, and TSS was lower than values reported in

the literature, with removal efficiencies of 43%, 36%, and 26%, respectively. This was attributed to operational control limitations, the current condition of the facilities, and primarily the design of the three-phase separator, which may allow solids to escape along with the effluent.

Regarding biogas yield, the production behavior was temporally variable, periodic, and non-stationary, with peak flows occurring between 7–8 a.m. and 11 p.m.–12 a.m., directly influenced by local conditions. The biogas composition presented an average methane concentration of 81%. A negative correlation was observed between influent flow rate and biogas flow, likely due to sewage dilution and reduced HRT when the influent flow increased.

The average concentration of dissolved methane in the effluent was $13.40 \pm 3.85 \text{ mg L}^{-1}$, representing a loss of 43%. The theoretical concentrations of dissolved methane, calculated using Henry's Law, showed little variation, resulting in oscillations in the saturation degree (0.32 to 1.28) that generally followed the trends of the experimentally measured concentrations.

The influent sewage variables that showed the strongest correlations with biogas production were COD ($p = 0.590$, moderate), alkalinity ($p = 0.450$, moderate), VSS ($p = 0.624$, strong), TSS ($p = 0.579$, moderate), and temperature ($p = 0.534$, moderate). In contrast, for dissolved methane, influent and effluent parameters showed weak or non-statistically significant correlations, indicating the need for further studies to better understand this important methane fraction, which is often lost in wastewater treatment plants.

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The authors have stated that there is no conflict of interest.

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