Biological desulfurization of biogas by a controlled aeration system

Dessulfuração biológica do biogás através de um sistema de arejamento controlado

Dessulfuración biológica de biogás mediante un sistema de aireación controlado

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ABSTRACT
The excessive demand of modern society for resources implies the need for development, propagation and use of energy sources more interesting from the environmental and economic point of view. Biogas is a potential alternative, originating from anaerobic degradation composed essentially of methane (CH4), carbon dioxide (CO2) and traces of other gases such as hydrogen sulfide (H2S) and moisture. To enable its use, a purification process is necessary, especially with regard to H2S, since it has characteristics that cause corrosion of equipment and toxicity to human health. This study aims to implement a biological desulfurization system for biogas generated from the anaerobic digestion of the effluent treatment system in an egg processing company. Both the monitoring of the biogas composition and the control of air injection into the system were performed automatically from a device from the manufacturer Awite, which proved to be interesting for full-scale applications. The system showed removal efficiency of up to 71.63% (June 17th) in the concentration of H2S at the exit of the biodigester when the extreme values obtained were used, and removal of 61.23% when the selected period was considered. Still, the temperature behavior was shown to influence the variable [H2S] in a directly proportional way. However, it was noticeable the restriction of the efficiency of the technique especially due to the low content of solids in the effluent and a need for adaptation in the engineering of the reactor.

Keywords: biogás, H2S removal, biological desulfurization, aeration system.

RESUMO
A demanda excessiva de recursos da sociedade moderna implica a necessidade de desenvolvimento, propagação e uso de fontes de energia mais interessantes do ponto de vista ambiental e econômico. O biogás é uma alternativa potencial, decorrente da degradação anaeróbica composta essencialmente de metano.
(CH4), dióxido de carbono (CO2) e vestígios de outros gases, como sulfeto de hidrogênio (H2S) e umidade. Para permitir a sua utilização, é necessário um processo de purificação, especialmente no que diz respeito ao H2S, uma vez que possui características que causam corrosão do equipamento e toxicidade para a saúde humana. Este estudo tem como objetivo implementar um sistema de dessulfuração biológica para biogás gerado a partir da digestão anaeróbica do sistema de tratamento de efluentes em uma empresa de processamento de ovos. Tanto o monitoramento da composição do biogás como o controle da injeção de ar no sistema foram realizados automaticamente a partir de um dispositivo do fabricante Awite, que se mostrou interessante para aplicações em larga escala. O sistema mostrou eficiência de remoção de até 71,63% (17 de junho) na concentração de H2S na saída do biodigestor, quando foram utilizados os valores extremos obtidos, e remoção de 61,23%, quando considerado o período selecionado. Ainda assim, o comportamento da temperatura mostrou influenciar a variável [H2S] de forma diretamente proporcional. Percebeu-se, no entanto, a restrição de eficiência da técnica, em especial devido ao baixo teor de sólidos no efluente e à necessidade de adaptação na engenharia do reator.

Keywords: biogás, remoção de H2S, dessulfuração biológica, sistema de aeração.

RESUMEN
La excesiva demanda de recursos por parte de la sociedad moderna implica la necesidad de desarrollo, propagación y uso de fuentes de energía más interesantes desde el punto de vista ambiental y económico. El biogás es una alternativa potencial, originada por la degradación anaerobia compuesta esencialmente de metano (CH4), dióxido de carbono (CO2) y trazas de otros gases como el sulfuro de hidrógeno (H2S) y la humedad. Para permitir su uso, es necesario un proceso de purificación, especialmente en relación con el H2S, ya que tiene características que causan corrosión de los equipos y toxicidad para la salud humana. El objetivo de este estudio fue implementar un sistema de dessulfuração biológica para biogás generado a partir de la digestión anaeróbica del sistema de tratamiento de efluentes en una empresa procesadora de huevos. Tanto la monitorización de la composición del biogás como el control de la inyección de aire en el sistema se realizaron automáticamente desde un dispositivo del fabricante Awite, que resultó interesante para aplicaciones a gran escala. El sistema mostró una eficiencia de remoción de hasta 71,63% (17 de junio) en la concentración de H2S a la salida del biodigestor cuando se utilizaron los valores extremos obtenidos, y remoción de 61,23% cuando se consideró el período seleccionado. Sin embargo, se demostró que el comportamiento de la temperatura influye en la variable [H2S] de manera directamente proporcional. Sin embargo, se evidenció la restricción de la eficiencia de la técnica, debido especialmente al bajo contenido de sólidos en el efluente y a la necesidad de adaptación en la ingeniería del reactor.

Keywords: biogás, remoción de H2S, dessulfuração biológica, sistema de aireación.
1 INTRODUCTION

Modern society uses resources in a way never seen before, and one of the points of greatest impact refers to the consumption by a variety of energy sources (Güney, 2019; Melnyk et al., 2020; Wang et al., 2022; Hassan et al., 2023). With the intention of getting rid of conventional energy sources, renewable sources have become increasingly interesting, especially from an environmental standpoint by replacing fossil fuels, which besides being responsible for greenhouse gas emissions in the atmosphere, also represent about 80% of the world's energy matrix and are considered a finite source, with durability estimated in four decades for some fuels (Abas et al., 2015).

Biogas is a gas originating from the anaerobic degradation of organic matter, consisting of a mixture of gases, which can be generically described by 60% methane (CH$_4$), 40% carbon dioxide (CO$_2$) and traces of other gases, such as hydrogen sulfide (H$_2$S) and moisture (Dalpaz et al., 2020). In this degradation process, microbial activity and variables such as pH, temperature and the type of substrate used are important variables in terms of controlling the process (Karlsson et al., 2014). According to CiBiogás, the potential for biogas production in Brazil adds up to 84.6 billion cubic meters per year, a volume which would be capable of supplying 40% of the national internal demand for electricity (Wang et al., 2022). However, in 2021 the production reached only 3% of this potential, showing that there is a huge room for growth in the sector (CiBiogás, 2022).

Regarding the brazilian state of Rio Grande do Sul (RS), locations of favorable biomass origin were mapped for the use of biogas and biomethane, which are considered the best alternative in the short term to meet the growing demand for energy and fuel in Rio Grande do Sul (Konrad et al., 2016). In general, biogas has a number of advantages in the economic, social, and environmental spheres, most notably the fact that it is a renewable energy source, and its source process can provide the treatment of inputs during treatment and produce digestate, which is an organic fertilizer with the potential to replace chemical fertilizers in sustainable agriculture (Kabeyi and Olanrewaju, 2022) which are still widely used in Brazil.
However, for biogas to be used as a source of mechanical, electrical and thermal energy and for biomethane production, it is necessary to introduce a previous step to produce a concentrated biomethane product with a quality similar to natural gas (i.e., Synthetic Natural Gas or SNG). The goal of this step is the removal of the impurities capable of causing low combustion efficiency (such as CO\textsubscript{2}) as well as the trace elements that may incur in high costs associated with equipment corrosion (e.g. hydrogen sulfide, H\textsubscript{2}S) (Kunz et al., 2022; Cavaler et al., 2021).

The presence of H\textsubscript{2}S in biogas can cause problems related to corrosion of equipment with which the gas comes in contact, which generates excessive maintenance costs (Cristiano et al., 2020; Maizonnasse et al., 2023; Haosagula et al., 2021).

In this work we focus on the removal of H\textsubscript{2}S, a colorless, toxic and flammable gas, capable of degrading facilities, engines and pipes to which it is subjected (Marques, 2020). The production range of this gas depends especially on two factors: the amount of sulfur-containing compounds available in the substrate and the sulfur-reducing and methanogenic microorganisms that compete for the same substrates (Nyamukamba et al., 2022; Promnuana and O-Thong, 2017). Specifically regarding the effects on human health, it is verified that contact with low concentrations (15-50 ppm) causes irritation of the mucosa in the respiratory tract, headaches, dizziness, and nausea, and this condition can be aggravated if the concentrations are higher, which can cause respiratory arrest (200-300 ppm) or even death (higher than 700 ppm) (Kunz et al., 2022). In this sense, the processes responsible for removing this gas are known as desulfurization processes, which can occur during or after the anaerobic digestion stage, and are characterized as biological, physical or chemical (Ryckebosch et al., 2011). The main desulfurization techniques are shown in Table 1, along with their respective advantages, disadvantages and associated efficiencies (Becker et al., 2022). However, it is noteworthy that few articles were found that focus on biological desulfurization of biogas generated from effluents with low solids concentration, which indicates the novelty of this study.
Table 1 Overall advantages and limitations of the desulfurization techniques.

<table>
<thead>
<tr>
<th>Desulfurization process</th>
<th>Advantages</th>
<th>Limitations</th>
<th>Efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical scrubbing (adsorption and absorption techniques)</td>
<td>Reliable and effective technologies, potential in the use of adsorption as final polishing in hybrid processes. Some sorbents are made of abundant and locally available materials, and some can be applied as fertilizers after use.</td>
<td>Requires the consumption of a sorbent and consequent disposal of the spent material. Possible formation of by-products. Performance may be affected by operating conditions and humidity.</td>
<td>Over 80% for an inlet concentration up to 2,000 ppm.</td>
<td>Becker et al. (2022)</td>
</tr>
<tr>
<td>Aerobic and anaerobic biotrickling filters (BTFs)</td>
<td>Small environmental impact, cost-effective operation, easier operational control, satisfactory results with alkaline pH and can operate with high H₂S inlet concentrations at high flow rates.</td>
<td>A previous inoculation stage is required. Oxygen availability and mass transfer could become a limiting factor; air supply may dilute biomethane; possibility of uneven distribution of the reactants. Drainage of the slurry must be provided.</td>
<td>Over 90% for H₂S inlet concentrations up to 5,000 ppm.</td>
<td>Becker et al. (2022), Chaiprapat et al. (2015)</td>
</tr>
<tr>
<td>Anoxic desulfurization</td>
<td>Simple and with low maintenance. The high solubility of the nitrate in anoxic conditions does not limit the mass transfer, avoids the biogas dilution and the explosion risks.</td>
<td>The need for an electron acceptor source could increase the operating costs, but this source could be substituted by nitrate-rich wastewater.</td>
<td>Over 80% for inlet concentrations ranging from 1,200 to 6,000 ppm.</td>
<td>Becker et al. (2022)</td>
</tr>
<tr>
<td>Aeration and air injection</td>
<td>Low cost and simple construction. Simplest of the biological methods. Suitable and cost effective. Improves COD and volatile suspended solids when used to treat wastewater. Precipitated S₀ is removed with digested sludge. No pretreatment of air is necessary.</td>
<td>It is necessary to maintain adequate levels of O₂. Optimal process control needed with variable air/oxygen dosing rate. Sulfur deposition can cause clogging of gas pipes. Risks of explosion when mixing CH₄ and O₂. Possible formation of sulfur mats in the digester's headspace.</td>
<td>90% or higher for inlet concentrations between 2,000 and 4,000 ppm.</td>
<td>Becker et al. (2022), Mulbry et al. (2017), Jeniček et al. (2017) Choudhury et al. (2019)</td>
</tr>
</tbody>
</table>
In general, biological processes have been gaining prominence in the gas treatment scenario, especially due to their advantages such as simple operation, low cost, and sustainability (Das et al., 2022). Becker et al. (2022) reviewed recent studies on technologies for biogas desulfurization and concluded that biological and microaeration processes seem to give the best results when considering that good performance means removal efficiency above 99% for inlet concentrations higher than 2,000 ppm H₂S. Aeration is considered an interesting technique since it allows both the oxidation of H₂S to elemental sulfur and prevents the reduction of sulfur into H₂S. According to Jeniček et al. (2017) this process consists of the controlled dosage of a certain concentration of oxygen in the biodigester so that the oxidation of sulfide into elemental sulfur occurs. For this, a number of sulfur-oxidizing microorganisms are used, most of which are autotrophic, that use the CO₂ present in the biogas as a carbon source and therefore have the potential to improve the biogas production rate and composition from the anaerobic digestion process (Nghiem et al., 2014), as well as providing improved hydrolysis, methane production, production of volatile fatty acids (VFAs) to remove hydrogen sulfide and control process stability (Nguyen and Khanal, 2018). Depending on the required sulfide levels for the end use of the biogas, the use of an additional removal technology may be unavoidable. However, in these cases microaeration is still seen as an advantageous pre-treatment in the sense of improving the traditional technology that follows it, increasing its lifetime (Muller et al., 2022).

In this context, this study aims to implement a biological desulfurization system for biogas generated by an egg processing company using a biodigester aeration system. This system makes it possible to monitor and reduce the concentrations of hydrogen sulfide, which guarantees an improvement in both human health and the integrity of the metallic structures in the company’s facilities.
2 MATERIALS AND METHODS

2.1 DESCRIPTION OF THE CASE STUDY

The enterprise is characterized as a company in the food industry, acting in the processing of eggs and egg products located in Southern Brazil. As wastewater treatment, the plant constructed an anaerobic lagoon with dimensions of 60 x 20 m, with a depth of 5.5 m.

The average flow of effluent generated in the company is 353 m³/day, and it is characterized in Table 2 according to the characteristics of the entrance and exit of the anaerobic lagoon.

The biogas is generated in the anaerobic lagoon at a flow rate of approximately 5 m³/h. As shown in Table 2, it is verified that 85% of BOD and COD removal occurs from this lagoon, being considered a good efficiency load removal. In addition, other parameters showed efficiency in the treatability, however it is highlighted that the focus is the visualization of the desulfurization that happens in this same environment.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inlet effluent</th>
<th>Outlet effluent</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BODs (Biological Oxygen Demand)</td>
<td>1,740.6</td>
<td>281.4</td>
<td>mg/L</td>
</tr>
<tr>
<td>Volatile organic acids</td>
<td>402.0</td>
<td>252.0</td>
<td>mg/L</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>861.8</td>
<td>1,433.0</td>
<td>mg/L</td>
</tr>
<tr>
<td>COD (Chemical Oxygen Demand)</td>
<td>4,453.2</td>
<td>727.1</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulfides</td>
<td>6.18</td>
<td>5.76</td>
<td>mg/L</td>
</tr>
<tr>
<td>TSS (Total Suspended Solids)</td>
<td>0.28</td>
<td>0.17</td>
<td>%</td>
</tr>
<tr>
<td>VSS (Volatile suspended solids)</td>
<td>82.47</td>
<td>56.66</td>
<td>%</td>
</tr>
<tr>
<td>pH</td>
<td>8.67</td>
<td>7.34</td>
<td>-</td>
</tr>
</tbody>
</table>

Source: Data Processed by Researchers
2.2 IMPLEMENTED BIOLOGICAL DESULFURIZATION SYSTEM

The desulfurization system implemented for the purification of biogas consists of a mobile laboratory belonging to the Center for Research in Sustainable Energy and Technology (CPETS), located in the Taquari Valley Science and Technology Park (Tecnovates), at the University of Vale do Taquari (Univates). The system is composed of flow equipment (Awiflow), desulfurization (AwiDesulf) and quality (Awiflex) of biogas, from the manufacturer AwiTE. Its operation consists of injecting air into the biodigester and evaluating the composition of the biogas in an automated way. In addition, the two last pieces of equipment operate together in the sense that, from the reading taken by Awiflex, AwiDesulf responds by injecting more air into the system or stopping the dosage, according to the values obtained for O$_2$ and H$_2$S (Fig. 1). With regard to the energy demand of the process, the required blower power is 0.37 kW.

The flow equipment was installed in the gas network and centralized in the inner part of the pipe, with a flow velocity that could vary in the range of 0.3 to 15 m.s$^{-1}$. The desulfurization process was carried out from the automatic regulation of air injection through a PI controller (proportional and integral) associated with a superior controller of fuzzy logic. Thus, the equipment promotes biological desulfurization by automatically triggering the injection of air in the biodigester according to the current values of gas analysis. The control margin is maintained between 0 and 1 % of O$_2$, depending on the concentration of H$_2$S measured and with a deactivation threshold of 2.4 % of O$_2$. Finally, the analysis of the biogas composition was performed by individual sensors of the equipment and relative to the following parameters: CH$_4$, CO$_2$, O$_2$, H$_2$ and H$_2$S (Table 3).
Table 3 Awiflex equipment evaluation parameters and respective sensors.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Measuring Principle</th>
<th>Measuring Range</th>
<th>Repeatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH₄)</td>
<td>Dual beam infrared sensor</td>
<td>0 - 100 Vol.-%</td>
<td>± 0.2%</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>Dual beam infrared sensor</td>
<td>0 - 100 Vol.-%</td>
<td>± 0.2%</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>Electrochemical</td>
<td>0 - 25 Vol.-%</td>
<td>± 0.1%</td>
</tr>
<tr>
<td>Hydrogen sulfide (H₂S)</td>
<td>Electrochemical</td>
<td>0 - 5,000 ppm</td>
<td>± 1%</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>Electrochemical</td>
<td>0 - 2,000 ppm</td>
<td>± 1%</td>
</tr>
</tbody>
</table>

Source: Awite (2022).

Regarding air injection points, these were pre-established at the moment of the lagoon construction, having as objective that its positioning was on the opposite side of the biogas outlet, so that there was no possibility of changing these points. On the opposite side of these points the flow meter was installed and a collection point was defined in this pipe for the analysis of the composition of the biogas at the outlet of the biodigester (Fig. 1).

2.3 DATA COLLECTION AND ANALYSIS

Regarding data collection from the mobile laboratory, the total evaluation period was from May 26th to July 7th. However, the data collection itself did not occur every day, but was limited to the following schedule: 3 days without the blower, followed by 24 with the blower on, and finally 5 more days with the blower off. The reading was automated, with hourly measurements. To expand the analysis where the blower was not present, two more collections were made at the exit point of the biodigester in metalized bags for further analysis by gas chromatography in the Clarus 580 GC equipment, from the manufacturer PerkinElmer, equipped with a Photometric Flame Detector (FPD) for the
identification of H₂S and with a Thermal Conductivity Detector (TCD) for reading CH₄, CO₂, H₂, O₂ and N₂.

Figure 1. Schematic drawing of (a) the superior view of the system and (b) the front view of the reaction that occurs in the anaerobic lagoon.

The hourly data collected during the 41 days were analyzed by a Multiple Linear Regression analysis. This analysis was applied to verify the influence of the independent variables (methane, carbon dioxide and oxygen concentration; biogas temperature and flow rate) on the dependent variable (hydrogen sulfide concentration). With the exception of the flow rate variable, all other independent variables were significant in the construction of the model. Additionally, correlation graphs were organized to visualize the trends of the independent
variables in relation to the outcome variable. The analyses were carried out in the Past 4.03 program (Hammer et al., 2001).

3 RESULTS AND DISCUSSION

The inlet effluent is the result of its passage through the reactor where acidogenesis occurs - the second stage of the anaerobic digestion process. This effluent presents low concentration of total solids (0.28%) and high concentration of volatile solids (82.47%), indicating that the effluent is of good degradability. With respect to the effluent leaving the anaerobic lagoon, one notices the decrease of both concentrations: 0.17% of TSS and 56.66% of VSS. The retention time longer than necessary of the effluent allows a more efficient degradation, which enables the generation of biogas with high concentrations of CH₄.

The raw effluent of the company has a COD/BOD ratio equivalent to 2.43, being characterized as of good degradability and easily treated by biological processes according to Braga et al. (2012), who infer that an effluent that has this ratio below 2.5 is considered easily biodegradable. The calculated effluent retention time was 18.7 days.

The retention time of the biogas in the gasometer (the dome of the biodigester) was calculated as 10 days, which refers to the permanence time of the gas in the biodigester and, consequently, the time necessary for the integral exchange of the gaseous volume in the gasometer.

From the biogas composition analyses, the influence of the micro-aeration system throughout the evaluated period was verified. Fig. 2 presents the variation of the concentration of the following components: CH₄, O₂, CO₂ and H₂S.
Regarding the methane concentrations observed throughout the evaluated period, it was found that these remained without significant variations, with an average of 83.84%. The maximum concentration value was reached on the 30th day (87.4%), while the minimum was verified on the 34th day (79%). According to Huertas et al. (2020), the concentration of methane tends to decrease as the micro-aeration occurs due to the presence of nitrogen gas (N₂) from the air, as seen in Fig. 3. There was also a decrease in the concentration of CH₄ on day 33, which cannot be attributed to the variation of any of the parameters evaluated, possibly resulting from a variation in the composition of the effluent.
Mendonça, Otenio and Paula (2021) infer that the non-occurrence of the acidification stage in the reactor provides stability to methanogenesis. Thus, the existence of an acidification pond prior to the anaerobic pond where the aeration system was implemented (analysis reactor) contributes to the biogas generated in this second pond presenting higher methane concentrations. In this sense, the high concentrations of CH$_4$ observed reveal a reality different from what is preached in the literature and tests performed by this research team. Systems that consist of the physical separation of the stages related to acidification and methanogenesis provide the optimization of the processes separately with respect to the production of H$_2$ and CH$_4$, so that this division ensures greater stabilization of the process when compared to single-stage systems for methane production. This concept is based on the fact that the production of these different gases occurs mostly in different pH ranges and with different hydraulic retention times (Sá et al., 2014).

The carbon dioxide presented an average of 15.37% throughout the evaluated period, with maximum value of 18.62% on day 34 and minimum of 13.54% on day 28 – the first day after removal of the aeration system. From Fig. 4 it was possible to observe the inversely proportional behavior between the variables CO$_2$ and CH$_4$. 

![Figure 3. Relationship between methane and oxygen concentrations in biogas.](source)
Figure 4. Relationship between methane and carbon dioxide concentrations in biogas.

Source: Data Processed by Researchers

The transformation that occurs regarding sulfur is from H₂S to elemental sulfur (S₀), with only the transformation capacity of H₂S to elemental sulfur being calculated as a function of the presence of injected oxygen in the system. In regard to the H₂S concentrations verified throughout the evaluated period, an average of 1,645.46 ppm was obtained. From this value one can see the need for a complementary process, since the generators commonly used to generate electricity have a limit of 200 ppm H₂S. From the extreme values obtained in the period before the aeration system and in the period of air injection, it was verified the removal of 71.63% of this gas, considering that in the first measurement point the concentration of 2,677.78 ppm of this gas was verified. However, from the estimated time necessary for the integral exchange of biogas inside the biodigester, an interval of 10 days was obtained, which implies the period evaluated with the blower. Therefore, evaluating the average of the period that begins ten days from the tenth day of air injection in relation to the previous (without the presence of the blower), there was a decrease of 61.23% in the concentration of this component. In relation to both scenarios presented, there was an increase in the concentration of this gas after the removal of the aeration system, reaching 2,866.42 ppm in the last measurement taken. The trend of decrease followed by increase expresses the direct influence of aeration in the biodigester on the quality of the biogas.
In Fig. 5 a relationship between biogas temperature and hydrogen sulfide concentration is observed. However, due to the fact that the daily Delta T (ΔT) values in the evaluated period were considerably high, it was decided to select a shorter period for the evaluation of the hourly variation of temperature. For a better understanding of the relationship between biogas temperature (a consequence of the ambient temperature) and the concentration of H₂S in the sample, a cutout consisting of considerable temperature variations was used for a better visualization of this relationship (Fig. 6). For this, one of the peaks of biogas temperature variation was selected. More specifically, the period from June 26th to June 28th was chosen because this period presented an increase in temperature, followed by stability and decrease, therefore being considered representative for the evaluation of the influence of temperature on the concentration of H₂S.

During the three days (June 26 to 28) there was an increase in the concentration of the gas, which coincided with the increase in temperature, especially noticeable in the measurements taken near noon time on 6/27 and 6/28, when the temperature reached higher values, reaching 23.6 °C (at 12:00) and 23.2 °C (at 10:00). Concomitantly, it was found that the concentration of H₂S reached the following values: 1,419.76 ppm and 1,365.85 ppm, respectively. It
can be seen that the second H$_2$S peak was less pronounced when compared to the first, which can be explained by the fact that the concentration of the gas had suffered a sharp drop a few hours earlier (June 28 at 6:00 am, with 1,248.06 ppm), which may have caused its increase four hours later to be more subtle.

Choudhury et al. (2019) found a rapid decrease in H$_2$S concentration that was attributed to the temperature drop in the unheated digester at that time (comparison between outdoor temperatures in summer and winter).

Figure 6. Cutout of the relationship between H$_2$S concentration and biogas temperature.

![H$_2$S concentration and biogas temperature](source: Data Processed by Researchers)

Regarding the statistical analysis, the Multiple Regression model proved to be significant ($F = 637.83; p < 0.0001; R^2 = 81.17\%$). When hourly data were used, the dependent variables (CH$_4$, O$_2$, CO$_2$, biogas temperature and biogas flow rate) explained 81.17% of the behavior of the dependent variable H$_2$S. The correlation coefficients were significant for O$_2$ ($p < 0.0001$), CO$_2$ ($p < 0.0001$), temperature ($p = 0.0292$) and flow rate ($p < 0.0001$) and not significant for CH$_4$ ($p = 0.1009$) (Fig. 7).

The relationship between the concentration of H$_2$S and the other constituents of biogas, in addition to the flow and temperature was also evaluated. It can be seen from the linear trend lines that methane concentration, oxygen and biogas flow rate are inversely related to H$_2$S, while carbon dioxide concentration and biogas temperature are directly related.
Figure 7. Variation of H$_2$S concentration as a function of the variables (a) methane concentration, (b) oxygen concentration, (c) carbon dioxide concentration, (d) biogas temperature and (e) biogas flow.

As verified in the statistical analysis, the negative correlation between the presence of H$_2$S and O$_2$ in the biogas indicates that these variables are inversely related, which corroborates the premise of the micro-aeration technique. Fig. 8 shows that, as the oxygen concentration in the biogas increased (as a function of the dosage of air in the biodigester), there was a decrease in the concentration of hydrogen sulfide.
Considering that when the blower is on, 50 m³/h (833.3 L/min) of air is injected into the biodigester, it was verified that from the aeration start date a considerable increase in the oxygen concentration in the biogas occurred, which reached its maximum value of 1.32% on the 8th day of air injection. No dilution effects were observed because only a small amount of air was injected compared to the volume of air contained in the biodigester.

Díaz et al. (2011) obtained efficiencies higher than 98% in H₂S reduction when implementing a microaeration system, Jeníček et al. (2017) achieved values between 74% and 99%, Krayzelova et al. (2014) verified an average removal of 73% in a Upflow Anaerobic Sludge Blanket (UASB) reactor. Considering that the residence time of biogas in the headspace and the available surface are the main factors that affect the efficiency of hydrogen sulfide removal through sulfur oxidation in the headspace (Krayzelova et al., 2015), it is believed that the results obtained in this study are attributable especially to the low value of total solids of the effluent, so that the need for measures that favor greater removal of this gas is perceived. In this sense, it is proposed the adoption of a complementary biogas purification technology, depending on its final use. Furthermore, as an alternative in loco the possibility of installing a grid inside the biodigester to increase the contact area for the microorganisms involved in the oxidation of H₂S is raised, since the low solid content of the effluent does not play
a favorable role for the fixation of this microbiota. Finally, as a proposal for adaptation of the reactor engineering, it is suggested to modify the air injection and gas collection points, allowing longer contact time of the oxygen with the H\textsubscript{2}S.

4 CONCLUSIONS

The aeration system in the biodigester showed a positive response in relation to the reduction of hydrogen sulfide concentration from the increase of oxygen concentration present in the biogas. However, it was noticeable the restriction of the efficiency of the technique especially due to the low content of solids present in the effluent, for which three solutions are proposed: the use of a complementary biogas purification technology, the installation of a grid inside the biodigester to increase the area of contact of the biogas with the microbiota that removes H\textsubscript{2}S and the change of the points of air injection and gas collection in the biodigester.

In addition, the direct proportional relationship between biogas temperature (a consequence of ambient temperature) and hydrogen sulfide concentration was verified by observing hourly data that presented considerable temperature variations.

The tests were carried out on a large scale, from which it was possible to verify the technical feasibility of future implementation of a fixed system at the company’s premises.

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