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Occurrence of siloxanes in biogas produced in UASB reactors treating mainstream sewage

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Highlights:

- The concentration of eight siloxanes in biogas from UASB reactors was investigated;
- The results indicated that biogas from UASB reactors and sludge digesters are similar in composition;
- Total siloxanes concentration in the biogas from UASB reactors were 2.7 times lower than the values reported for sludge digesters;
- This work brought the first results on the occurrence of siloxanes in biogas from UASB reactors.

Keywords: Energy recovery; Siloxanes; Impingers.

INTRODUCTION

Biogas produced in Sewage Treatment Plants (STPs) contains siloxane, a volatile organic compound present in various household products, such as cosmetics and personal hygiene items [1, 2]. Siloxanes can be divided into two groups according to their molecular structure: linear and cyclic siloxanes, represented by the terms Lx and Dx, respectively. The letter "x" indicates the amount of silicon atoms in the molecular structure. Most siloxane characterization studies are related to biogas generated in sludge digesters, we found only one study on the occurrence of siloxanes in biogas from anaerobic reactors treating mainstream sewage [3]. This was somehow expected, since the interest in the removal of siloxanes from biogas only occurs when energy recovery is intended and, as a rule, this is most practiced in countries where biogas is produced in sludge digesters. Problems related to the presence of siloxanes in biogas is due to its transformation into silicon dioxide during combustion, since these are solid compounds that cause abrasion of the moving parts of the power generation system [1]. Therefore, energy recovery from biogas is conditioned to meeting the siloxane limits required by the manufacturers of energy conversion equipment [4]. Hence, the present work sought to investigate the occurrence of siloxanes in the biogas from UASB reactors treating mainstream sewage, in order to generate information that can contribute to the understanding of the feasibility of energy recovery from biogas produced in the huge park of anaerobic reactors in operation in Brazil.

METHODOLOGY

The experimental apparatus consisted of a demonstration-scale UASB reactor (V=14.2 m^3) fed on real wastewater (average flowrate of 44 $m^3.d^{-1}$) taken from the Arrudas STP (PE=1.5 million inhabitants), located in Belo Horizonte city, Minas Gerais, Brazil. The Arrudas STP features an aerobic wastewater treatment system utilizing a conventional activated sludge model and includes a set of 200 kW gas

turbines powered by biogas generated from sludge digesters. The treatment efficiency of the monitored UASB reactor was evaluated using conventional physicochemical parameters, while the composition and flow of biogas were monitored using portable equipment.

To sample siloxanes in biogas, the system illustrated in Figure 1 was used. The first three impingers were filled with 20 mL of HPLC/GC grade methanol and the last one remained empty to protect the sampling pump. The flow rate used was 100 $mL.min^{-1}$ and the sampling time was 90 minutes. The total monitoring period was five months, with an average sampling frequency of once a week. The eight siloxanes of interest (L2-L5 and D3-D6) were analyzed using a GC-MS (Thermo Scientific ISQ 7000).

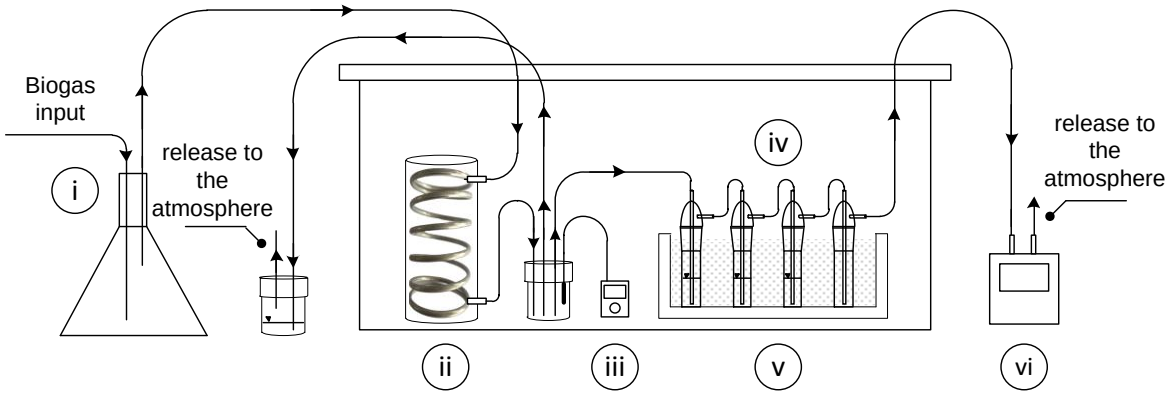

Figure 1: Biogas sampling apparatus using impingers: (i) reservoir for gas homogenization; (ii) copper coil to reduce gas temperature; (iii) digital thermometer for measuring gas temperature; (iv) set of four impingers; (v) ice bath and (vi) high-precision gas sampling pump.

RESULTS AND CONCLUSIONS

The performance and operational stability of the UASB reactor was typical and in accordance with that reported in the literature [5]. Like so, the results on siloxanes characterization can be considered representative of a UASB reactor treating sewage under normal operating conditions.

The main siloxanes present in the biogas of the UASB reactor were D4 and D5, representing on average 16% ± 3% and 83% ± 13% of the total, respectively (Figure 2a). The siloxanes L2, L3, L5 and D6 were identified in a smaller number of samples, between 3 and 12 of the 23 biogas samples collected, however the concentrations were below the limit of quantification of the analytical method, except for one sample for D6. The siloxane L4 was not found in any of the samples and siloxane D3 could not be accurately quantified due to chromatographic column bleeding problems. However, according to data in the literature, the concentration of this siloxane in biogas from STPs is not significant (Figure 2b).

According to the literature, the main siloxanes present in biogas from sludge digesters are D4 and D5, together representing more than 90% of the total (about 22% and 73%, respectively) (Figure 2b). Thus, in terms of the qualitative composition of siloxanes, the biogas from UASB reactors and sludge digesters are similar. This can be explained by the fact that cyclic siloxanes are predominant in personal care products, considered the main sources of these compounds in STPs [2].

The median concentration of total siloxanes in the biogas of the UASB reactor was 6.9 mg.m^{-3} (Figure 2c), about 2.7 times lower than the medians reported in the literature for sludge digesters (19 mg.m^{-3}) (Figure 2c). Regarding the concentration of siloxanes in biogas from sludge digesters of Brazilian STPs, an average value of 27.6 mg.m^{-3} was verified [6], a result about 4 times higher than that found in the biogas of the UASB reactor monitored in this study.

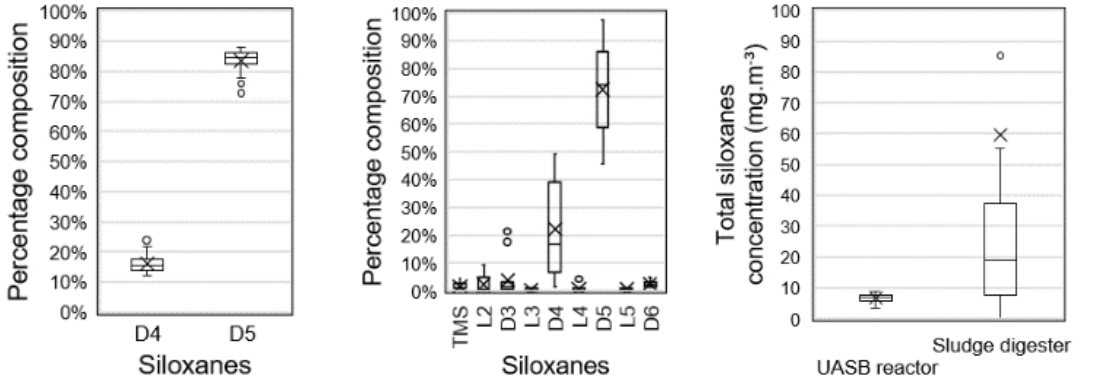

Figure 2: (a) Percentage composition of siloxanes in the biogas of the UASB reactor (present work); (b) Percentage composition of siloxanes in the biogas of sludge digesters (data from the literature); and (c) Total concentration of siloxanes in the biogas of the UASB reactor and sludge digesters. Number of data: (a) D4 = 23; D5 = 23; (c) UASB reactor = 23; sludge digesters = 37 (outliers with values above 100 mg.m^{-3}: 112.4; 127.4; 163.7; 361.7 and 812.8). Source: [4].

Overall, this study concluded that the cyclic siloxanes D4 and D5 were predominant in both the biogas from the UASB reactor treating mainstream municipal sewage and the biogas from the sludge digesters. However, the concentrations of total siloxanes in the biogas of the UASB reactor were much lower than those reported for biogas from sludge digesters.

Additionally, it is important to note that all measured concentrations were below the maximum limit allowed by manufacturers of internal combustion engines [4]. This finding could simplify and reduce the costs of biogas treatment and energy recovery in Brazil for STPs utilizing UASB reactors for mainstream sewage treatment and employing internal combustion engines for energy generation from biogas produced by these reactors. Nevertheless, considering that siloxane concentrations above 0.46 mg.m^{-3} pose a significant challenge for gas turbines (equipment used at the Arrudas STP) [4], an efficient treatment of biogas is essential, regardless of whether it originates from UASB reactors or sludge digesters.

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REFERENCES

1. Arepacochaga, N., Valderrama, C., Raich-Montiu, J., Crest, M., Mehta, S., & Cortina, J. L. (2015). Understanding the effects of the origin, occurrence, monitoring, control, fate and removal of siloxanes on the energetic valorization of sewage biogas: A review. *Renewable and Sustainable Energy Reviews, 52*, 366–381.
2. Horii, Y., & Kannan, K. (2008). Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. *Archives of Environmental Contamination and Toxicology, 55*(4), 701–710.
3. Eller, C. M. (2013). *Caracterização dos compostos traços influentes no aproveitamento energético do biogás gerado em reator UASB no tratamento de esgoto doméstico* (Master's thesis). Universidade Federal do Espírito Santo, Vitória.
4. Santos, J. M. B. (2023). *Ocorrência de siloxanos no biogás de reatores UASB e avaliação de procedimentos e parâmetros de amostragem* (Doctoral dissertation). Universidade Federal de Minas Gerais, Belo Horizonte.
5. Chernicharo, C. A. L., & Bressani-Ribeiro, T. (2019). *Anaerobic reactors for sewage treatment: Design, construction and operation*. IWA Publishing.
6. Martinez, S. J., Michel, R., Umemura, O. S., Rosseti, A. C., Panadés, P. H., Alvim, G. L., Ferreira, A. A., Castilho, D. C., Oliveira, B. A. P., & Coutinho, M. A. F. (2015). P194 – Amostragem e análise de biogás e biometano em aterros sanitários e ETEs.