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Characterization of siloxanes in biogas from UASB reactors treating sanitary sewage

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Highlights:

- Biogas is an energetic byproduct of anaerobic sewage treatment.
- The common contaminants in biogas include compounds of S, NH_3, P, siloxanes and Cl.

Keywords: UASB, Biogas, Siloxanes.

INTRODUCTION

The most common contaminants found in biogas include volatile compounds of silicon, S, P, Cl, CO, H_2S, NH_3, halogens, and siloxanes[1]. Additionally, volatile organic compounds (VOCs) like benzene, ethylbenzene, toluene, and xylenes (BTEX) are prevalent in biogas[2]. These contaminants pose challenges for energy valorization and environmental safety, necessitating purification processes to ensure the quality and safety of biogas for various applications[3]. The state of the art regarding siloxanes in biogas involves the evaluation of sampling methods, analysis techniques, and purification strategies. Various studies have highlighted the presence of siloxanes in biogas and their negative impact on energy applications. Studies also evaluate the impact of siloxanes on downstream components during biogas combustion, highlighting the formation of Si-based particles and their interaction with oxygen carriers that damage engine parts and present possible risks to health and the environment[3].

Research has focused on developing reliable sampling methods like impingers and adsorbent tubes, as well as analytical methods such as gas chromatography for quantifying siloxanes in biogas samples[2]. These advancements aim to address the challenges posed by siloxanes in biogas, ensuring the quality and usability of biogas as a renewable energy source[3].

The aim of this paper was the characterization of siloxanes in biogas from UASB reactors treating sanitary sewage.

METHODOLOGY

The biogas sampling process was carried out at 5 points on the wastewater treatment plant (WWTP), located in Curitiba (Brazil). Methanol was the solvent used for the 3-hour sampling, with a flow rate of 0.100 to 0.120L/min. Three impingers containing methanol were used for each point, and the samples were named according to the point and the number of the *impinger* used . The determination of siloxanes by gas chromatography and sampling with impingers was carried out using the method provided for by ABNT NBR 16560.

The samples were analyzed by gas chromatography coupled to mass spectrometry (GC/MS), with a fused silica capillary column (DB-5ms). The initial column temperature was 50 °C maintained for 4 min, then, the temperature was 180 °C using a heating rate of 15 °C min^{-1}, remaining for 2 min, and subsequently heated to 250 °C at 15 °C min^{-1} and maintaining up for 2 min. An injection of 1 μL of sample was performed, using the 1:10 split mode, and detection in SIM (Single Ion Monitoring) mode, monitoring the ions described in STANDARD ABNT 16560. Siloxanes are presented in linear or cyclic form represented by Lx and Dx, respectively, where X indicates the number of silicon atoms in the molecular structure.

The presence of 8 siloxanes was evaluated in the samples: Pentamethyldisiloxane (L1), Hexamethyldisiloxane (L2), Hexamethylcyclotrisiloxane (D3), Octamethyltrisiloxane (L3), Octamethylcyclotetrasiloxane (D4), Decamethyltetrasiloxane (L4), Decamethylcyclopentasiloxane (D5), and Dodecamethylpentasiloxane (L5).

RESULTS AND CONCLUSIONS

Table 1 presents the results of siloxanes obtained for the samples collected at the WWTP. Siloxanes L1, L2, and D6 were not observed in the analyzed samples, while siloxanes L3, L4, L5, D3, D4, and D5 were detected and quantified.The siloxanes D3, D4, and D5 were found for the analyzed samples and D4 was around 28-48% and D5 was around 50 to 70%. These results are in agreement with reported literature that indicate these siloxanes as the most found in biogas, representing about 90% of total siloxanes concentration[4].

The occurrence of these siloxanes is associated with the presence of personal care products, such as shampoo, conditioners, and creams in the sewage. The other siloxanes were present in traces below the LD and, in some cases, below the LQ.

The results indicate that for the production of biomethane from biogas it will be necessary to remove siloxanes to comply with legislation ANP 886 of 09/29/2022, whose limit is 0.3 mg of Si /m^3, in biomethane.

Table 1 - Concentration values of siloxanes and silicon in the samples analyzed in mg m^{-3} of biogas collected from the WWTP in Curitiba.

Points	Siloxanes (ng.mL^{-1})								Total silicon (mg m^{-3})
	L1	L2	L3	L4	L5	D3	D4	D5	
P1 - I1	nd	< LD	3.102< LQ	21.801 <LQ	< LD	255.669 < LQ	1630.212	1995.868	
P1 - I2	nd	< LD	nd	nd	< LD	398.287	83.977	< LD	
P1 - I3	nd	< LD	nd	nd	< LD	277.669 < LQ	33.656 < LQ	< LD	1.852
P2 - I1	nd	< LD	3.855 < LQ	17.552 < LQ	< LD	14.178 < LQ	1845.954	2778.121	
P2 - I2	nd	< LD	nd	nd	< LD	248.879 < LQ	46.679 < LQ	< LD	
P2 - I3	nd	< LD	nd	nd	< LD	319.489 < LQ	54.205 < LQ	< LD	2.302
P3 - I1	nd	< LD	1.959 < LQ	23.587 < LQ	40,65	< LD	1326.39	3237.685	
P3 - I2	nd	< LD	nd	nd	nd	86.278 < LQ	9.478 < LQ	< LD	
P3 - I3	nd	< LD	nd	nd	nd	< LD	< LD	< LD	2.412
P1 - I1	nd	< LD	3.125 < LQ	21.912 < LQ	nd	202.048 < LQ	1532.956	2252.9255	
P1 - I2	nd	< LD	nd	nd	nd	< LD	< LD	< LD	
P1 - I3	nd	< LD	nd	nd	nd	< LD	< LD	< LD	1.512
P2 - I1	nd	< LD	3.873 < LQ	21.751 < LQ	nd	19.716 < LQ	1652.548	1743.836	
P2- I2	nd	< LD	nd	nd	nd	46.279 < LQ	< LD	< LD	
P2 - I3	nd	< LD	nd	nd	nd	114.715 < LQ	15.277 < LQ	< LD	1.384

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