



## Presence of Siloxanes in the Biogas of a Wastewater Treatment Plant Separation in Condensates and Influence of the Dose of Iron Chloride on its Elimination

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### Abstract

The siloxanes present in the biogas produced during anaerobic digestion damage the mechanism of cogeneration equipment and, consequently, negatively affect the energy valorization process. For this reason, the detection and elimination of these silicon-derived chemical compounds are a priority in the management of cogeneration facilities. In this regard, the objectives of this paper are, firstly, to characterize the siloxanes in the biogas and, secondly, to qualitatively evaluate the influence of the dose of iron chloride on its elimination. The research was performed at the Rincón de León Wastewater Treatment Plant (Alicante, Spain). The outflow biogas of the digesters and of the pressurized gasometers was sampled and analyzed. The results obtained made it possible to demonstrate, firstly, the absence of linear siloxanes and that, of the cyclic siloxanes, the predominant type was decamethylcyclopentasiloxane, and, secondly, that the addition of iron chloride in the digesters significantly reduces the siloxane content in the biogas. Additionally, it was demonstrated that the process of compression of the biogas, with the elimination of condensates, also produces significant reductions in the concentration of siloxanes in the biogas.

**Keywords:** Anaerobic digestion; Biogas; Siloxanes; Energy valorization; Decamethylcyclopentasiloxane; Iron chloride

### Introduction

Methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) are the two main chemical compounds present in the biogas produced during anaerobic digestion in a Wastewater Treatment Plant (WWTP), their proportions varying between 50% and 70% for CH<sub>4</sub> and between 20% and 50% for CO<sub>2</sub>, depending on the performance of the process. The remaining percentage is mainly distributed between hydrogen (H<sub>2</sub>) (0-5%) and hydrogen sulfide (H<sub>2</sub>S) (0-1%) [1]. This biogas also contains numerous different chemical substances, in much smaller proportions, including carbon monoxide, ammonia, siloxanes, aliphatic and aromatic hydrocarbons, heavy metals, etc. [2].

The origin of the siloxanes in the biogas produced in a WWTP can be understood in view of the different uses and applications of silicon compounds. Obviously, the entry of this element and its chemical derivatives with the flow of wastewater determines its subsequent incorporation into the biogas, the treated wastewater and the sludge [3]. Many silicon-derived chemical compounds are used in many different areas of everyday life and industry, including basic oils used for cosmetic products (make-up, shampoos, creams, deodorants, etc.), foam inhibitors in detergents and cleaning products, alkaline earth metal cation chelating agents in detergent processes (zeolites), substances for the impregnation of paint in construction, products for cleaning leather and cars, excipients in medicines, microelectronic components, food additives, etc.

Cogeneration, that is, the production of electricity from the biogas generated in a WWTP, becomes considerably more complicated when the biogas contains organic silicon compounds. In the combustion of the biogas inside the engine, these gaseous silicon compounds are transformed into oxides which precipitate as solids on the inside of the machinery, eventually causing breakdowns and, finally, the total paralization of the cogeneration process. These oxides or precipitated

solids, which are highly abrasive, wear down the metal parts of the engine, significantly shortening the useful lifetime of the system.

The high concentrations of siloxanes or, in general, of organic silicon compounds in the inflow gases of the engines can produce silicones through combination with siloxanes under certain temperature and pressure conditions and the presence of components which favor polymerization, which are deposited in the form of a paste on the walls of the engines, impellers of the compressors, etc., which cause breakdowns in the generator as a result of the increased temperature and friction. Furthermore, given that they are combustible, if the organic silicon components reach the combustion chamber, they burn, producing the typical components of combustion, that is, CO<sub>2</sub> + H<sub>2</sub>O. The silicon also forms silica (SiO<sub>2</sub>) or silicates (RSiO<sub>3</sub>) which are partly eliminated with the exhaust smoke, but which are also deposited on the pistons, cylinders, spark plugs and, in general, all of the basic components of the engine. When the deposit is considerable, there are abrasion problems, ignition failure and even engine seizure. The mixture of the two effects mentioned above is the worst possible case, since the silicon paste is added to the particles of silica, forming a semi-rigid layer which has disastrous effects on cogeneration equipment.

Compounds to be found among the group of organic silicon

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compounds present in wastewater treatment plants (and landfill gases) include oxides with the general formula  $H_3Si-(O-SiH_2)_n-O-SiH_3$ . When the hydrogen atoms are substituted by organic remains, such as  $-CH_3$ , they become organic siloxanes. These organic siloxanes can be polymerized to become an organic polysiloxane called silicone. It has been discovered relatively recently that siloxanes can cause serious breakdowns in combustion engines [4-6]. The first serious problems to be documented were reported in Germany in 1989, in the cogeneration processes at the Dortmund-Huckarde landfill [7]. In the specific case of the cogeneration facilities in a WWTP, a large proportion of the problems caused in the engines are due, precisely, to the presence of siloxanes in the biogas produced during anaerobic digestion. In fact, abrasive incrustations have been found on the surface of the different mechanical parts of the machinery (valves, cylinder heads, pistons, exhaust systems, etc.) [8]. As has been stated, these solid deposits gradually wear down these components and, finally, cause a breakdown in the engine. The immediate consequence is the interruption of the cogeneration process and the collapse of the energy valorization system.

The cyclic and the linear siloxanes found in the biogas generated in a WWTP are: hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6), silanol (L1), hexamethyldisiloxane (L2), octamethyltrisiloxane (L3) and decamethyltetrasiloxane (L4) [2,9,10]. All of these siloxanes are practically insoluble in water, except trimethylsilanol [6]. Of the siloxanes entering a WWTP, 93.7% are in the form of D4 or D5 [11], later undergoing a high degree of volatilization during the treatment process, especially during aeration (58.6%), with another part (17.3%) remaining in the input sludge of the anaerobic digestion. It has been demonstrated that both D4 and D5 are found in the biogas of almost all WWTPs [5], while the remaining siloxanes appear in lower proportions (less than 10%). In particular, siloxane D6 (with a high molecular weight and low vapor pressure) does not appear in significant percentages, remaining in the sludge. The annexation of siloxanes to the biogas of the anaerobic digestion is favored by the increase in temperature during the process and by the relative volatility of siloxanes. Although there are several different procedures for the elimination of siloxanes from gaseous flows (liquid-gas absorption, solid-phase adsorption,  $CO_2$  condensation, filtering through membranes, condensation and indirect methods), the most widely-used method on an industrial scale is adsorption with activated carbon [12,13]. It should be noted, in this regard, that the regeneration of the adsorbent must be ruled out in small-scale applications for economic reasons, for operational simplicity and due to the difficulty of desorption of the siloxanes [14]. Among the disadvantages of this technique, related to the loss of performance, is the presence of other chemical substances in the composition of the biogas which may be retained on the surface of the carbon (competitive adsorption), limiting, and even preventing, the adsorption of the siloxanes. In particular, the humidity of the gases has a notable influence on the adsorption capacity of the carbon, reducing the siloxane elimination rate to such an extent that when relative humidity is greater than 50%, the capacity of the adsorbent is nil for the retention of siloxanes [15].

In practice, the indirect methods which are most commonly used to eliminate  $H_2S$  (oxidation of iron in limonite towers or the addition of iron chloride) also eliminate some of the siloxanes. Buch and Ingebrigtsen [16] claim that an  $H_2S$  adsorption tower with limonite -designed in principle only to remove sulfur from the biogas- also reduces the concentration of siloxanes by between 10% and 30%. Likewise, the addition of iron chloride ( $FeCl_3$ ) to the digesters to

eliminate  $H_2S$  can bring a certain removal of siloxanes through the polymerization of cyclic siloxanes, forming soluble substances which remain in the sludge. There is also a certain elimination of siloxanes in the condensates due to the high compression of the biogas in the storage process. ConzeptGmbH [4] and Reina [9] quantify the elimination of siloxanes related with his condensation at around 10%.

The Rincón de León WWTP (Alicante, Spain), suffered serious breakdowns in the electricity cogeneration system in 2002. There was a failure in the biogas combustion engines which caused the collapse of the energy valorization process. On dismantling the internal parts of the engines, deposits of abrasive incrustations were found on the surfaces of the different mechanical parts of the engine (valves, cylinder heads, pistons, exhaust system, etc.), as can be seen in Figures 1 and 2. It was clear that these solid deposits had gradually caused wear in the mechanical components, the detachment of material and, finally, the breakdown of the engine.

Suspecting that these incrustations may be originated by the presence of siloxanes in the biogas, wide-ranging research into this matter began [8]. This paper shows the results with respect to the composition of the outflow biogas from the digesters and the pressurized gasometers, with the objective of characterizing the siloxanes and quantifying their concentration, as well as determining the variation in those compounds as a consequence of the elimination of condensates during the compression process undergone by the biogas. The influence of the dose of  $FeCl_3$  in the digester on the elimination of siloxanes was also assessed.

There are not many investigations regarding to the siloxanes in biogas generated in the anaerobic digestion of the sludge of a WWTP, nor for any damages that may cause in the cogeneration process. This paper aims to fill the gap in this field.

## Materials and Methods

### Description of the Rincón De León Wwtp



**Figure 1:** Deposits on the generator valves.



**Figure 2:** Incrustation on valves and turbines.

The Rincón de León WWTP, which treats wastewater from the city of Alicante and the town of San Vicente Del Raspeig, is a conventional activated sludge plant using anaerobic digestion to treat the sludge, with energy valorization of the biogas by cogeneration. The energy recuperation system consists of: sludge heating (boilers and heat exchangers), gas storage (high-pressure gasometers and compressors), gas flares and a cogeneration system using biogas (auxiliary heat exchangers and generators).

For the biogas storage process, the biogas is compressed up to a pressure of 3 bars, which produces condensates. To measure the possible elimination of siloxanes from the condensate, the biogas produced in the anaerobic digester and the outflow biogas from the pressurized gasometer (the inflow gas of the generator) was sampled and analyzed.

### Reagents and adsorbents

The liquid solvents (of HPLC 2.5L chromatographic quality) used were n-Hexane, Tetradecane and Hexadecane. The products used as a base for the preparation of undiluted patterns for the determination of siloxanes, with purities expressed as a % (w/v), were: tetramethylsilane ((CH<sub>3</sub>)<sub>4</sub>Si), L1, 99.9%; octamethyltrisiloxane (C<sub>8</sub>H<sub>24</sub>O<sub>2</sub>Si<sub>3</sub>), L3, 97%; decamethyltetrasiloxane (C<sub>10</sub>H<sub>30</sub>O<sub>3</sub>Si<sub>4</sub>), L4, 97%; octamethylcyclotetrasiloxane (C<sub>8</sub>H<sub>24</sub>O<sub>4</sub>Si), D4, 97%; decamethylcyclopentasiloxane (C<sub>10</sub>H<sub>30</sub>O<sub>5</sub>Si<sub>5</sub>), D5, 97%; and dodecamethylcyclohexasiloxane (C<sub>12</sub>H<sub>36</sub>O<sub>6</sub>Si<sub>6</sub>), D6, 97%.

### Analytical methods

The analytical determination of siloxanes (in the gaseous samples and in the liquid patterns) was performed using gas chromatography techniques with mass spectrometry (GC/MS), following Standard Methods [17]. An HP/AGILENT TECHNOLOGIES 6890N gas chromatograph with a split/splitless capillary column inlet was calibrated and a DB-5.30 m chromatographic column was chosen, with 0.25 mm ID and 0.25 micra film. An AGILENT TECNOLOGIES 5973N mass spectrometer was used as a selective detector, with a source of electron ionization (EI).

For the characterization of the siloxanes, three sampling campaigns were performed over a period of three months (one per month). In each campaign, 12 samples were taken, making a total of 36, using an HP 7683 automatic sampler.

### Dose of FeCl<sub>3</sub>

In the WWTP studied, FeCl<sub>3</sub> was added for the desulfurization of the biogas, due to the specifications of the engines. Under the normal operating conditions of the digesters, the usual dose is 80 gr FeCl<sub>3</sub>/kg ms. During the first sampling campaign, this dose was maintained, during the second it was progressively reduced until none was added and in the third, none of the reagent was added at all. In this way, in the latter two campaigns, the effect of the dose of the reagent on the D5 concentration in the biogas produced could be observed.

### Results and Discussion

Tables 1-3 show the values of siloxane and H<sub>2</sub>S concentrations obtained in the three characterization campaigns and at the two sampling points (outflow of the digesters and outflow of the pressurized gasometers). In campaign 1, only the results for cyclic siloxanes D4, D5 and D6 are included, since neither linear siloxanes nor any other cyclic siloxanes were detected in any of the samples. Campaigns 2 and 3 were performed with the objective of assessing the influence of the

Sample n°	Outflow biogas of digesters			Outflow biogas of gasometers			
	D4 (mg/m <sup>3</sup> )	D5 (mg/m <sup>3</sup> )	D6 (mg/m <sup>3</sup> )	D4 (mg/m <sup>3</sup> )	D5 (mg/m <sup>3</sup> )	D6 (mg/m <sup>3</sup> )	H <sub>2</sub> S (ppm)
1	1.6	7.8	nd	nd	3.7	nd	< 100
2	4.4	7.2	nd	3.5	5.2	nd	< 100
3	2.6	5.6	0.2	1.0	8.7	nd	136
4	2.8	9.9	nd	1.2	5.7	0.4	125
5	1.1	10.5	0.1	nd	8.8	nd	< 100
6	2.2	7.0	nd	nd	4.7	nd	< 100
7	nd	14.3	nd	nd	11.0	nd	103
8	1.5	6.6	nd	nd	8.2	0.2	118
9	nd	6.0	0.3	nd	5.5	nd	< 100
10	1.7	8.0	nd	1.6	7.0	nd	< 100
11	1.3	7.1	0.2	nd	5.5	nd	110
12	nd	2.7	nd	nd	4.4	nd	< 100
Mean	1.6	7.7	0.1	0.6	6.5	0.1	
Stand. dev.	1.4	2.9	0.1	1.1	2.2	0.1	

nd = not detected (concentration below the detection limit of our analytical method: < 0.1 mg/m<sup>3</sup>)

**Table 1:** Concentrations of the siloxanes D4, D5 and D6 in the outflow biogas of the digesters and the outflow biogas of the gasometers, and H<sub>2</sub>S concentrations in the gasometers. Campaign 1.

Sample n°	Outflow D5 in digester (mg/m <sup>3</sup> )	Outflow D5 in gasometer (mg/m <sup>3</sup> )	Outflow H <sub>2</sub> S in gasometer (ppm)
13	4.3	3.9	100
14	4.1	4.3	210
15	6.3	6.0	280
16	11.1	10.4	420
17	9.7	9.9	470
18	15.4	8.8	610
19	3.1	4.7	740
20	11.1	7.7	750
21	11.3	7.0	930
22	13.3	12.8	1,420
23	11.3	10.3	1,500
24	15.7	14.0	1,500
Mean	9.7	8.3	
Stand. dev.	4.3	3.3	

**Table 2:** Concentrations of siloxane D5 in the outflow biogas of the digesters and the outflow biogas of the gasometers, and H<sub>2</sub>S in the gasometers. Campaign 2.

FeCl<sub>3</sub> dose on the siloxane content of the biogas. In these two sampling campaigns, only D5 was determined, as it is the main component, as seen below.

As can be observed, siloxane D6 was detected in 4 of the 12 samples (33.3%) of the outflow biogas of the digesters and its mean concentration was 0.1 mg/m<sup>3</sup>. D4 appeared in 9 of the 12 samples (75%) with a mean concentration of 1.6 mg/m<sup>3</sup>. D5 was present in all the samples (100%) and its mean concentration was 7.7 mg/m<sup>3</sup>. With respect to the mean values, D4 represents 17.0% of the total siloxane concentration at the outflow of the digester, D5 represents 81.9% and D6, 1.1%.

With respect to the outflow biogas of the pressurized gasometers, siloxane D6 was detected in only 2 of the 12 samples analyzed (16.7%) and its mean concentration was also very low, 0.1 mg/m<sup>3</sup>. D4 was present in 4 of the 12 samples (33.3%) and its mean concentration was 0.6 mg/m<sup>3</sup>. D5 appeared in all the samples (100%) with a mean concentration of 6.5 mg/m<sup>3</sup>. In terms of the mean values, D4 represents 8.3% of the total siloxane concentration at the outflow of the gasometer,

Sample nº	Outflow D5 in digester (mg/m <sup>3</sup> )	Outflow D5 in gasometer (mg/m <sup>3</sup> )	Outflow H <sub>2</sub> S in gasometer (ppm)
25	12.1	7.6	> 1,500
26	9.9	11.1	> 1,500
27	10.3	9.0	> 1,500
28	19.1	19.4	> 1,500
29	18.8	5.8	> 1,500
30	7.6	11.1	> 1,500
31	14.2	7.4	> 1,500
32	13.4	14.3	> 1,500
33	14.2	13.9	> 1,500
34	19.1	6.9	> 1,500
35	16.9	15.5	> 1,500
36	18.8	18.2	> 1,500
Mean	14.5	11.7	
Stand. dev.	4.0	4.6	

**Table 3:** Concentrations of the siloxane D5 (mg/m<sup>3</sup>) and H<sub>2</sub>S (ppm) in the outflow biogas of the digesters and in the outflow biogas of the gasometers. Campaign 3.

D5 represents 90.3% and D6, 1.4%.

Figure 3 shows the percentage distributions of the concentrations of the siloxanes D4, D5 and D6 in the outflow biogas of the digesters and the outflow biogas of the gasometers.

It can therefore be stated that D5 is, by far, the siloxane found in greater quantities in the biogas. Likewise, the results of this first campaign indicate that the process of compression of the biogas, with the elimination of condensates, produces significant reductions in siloxane concentrations. In the specific case of D5, the reduction was, on average, 15.6%.

Low concentrations of H<sub>2</sub>S were found in the digestion biogas, since, during the first campaign, as indicated above, the usual dose of FeCl<sub>3</sub> (80 gr FeCl<sub>3</sub>/kg ms) was used to desulfurize the biogas.

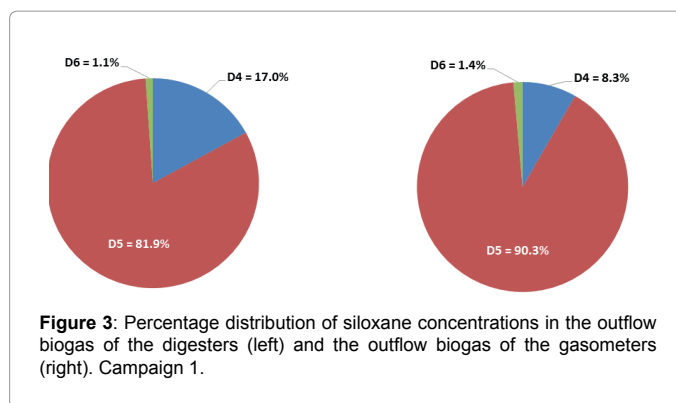
Figure 4 shows the distributions of values obtained in campaign 1 in the case of the siloxane D5 (the most significant), outflow of digesters and gasometers. As you can see, both fall roughly a normal distribution.

Campaigns 2 and 3 focused on siloxane D5, as it was the predominant compound in the biogas.

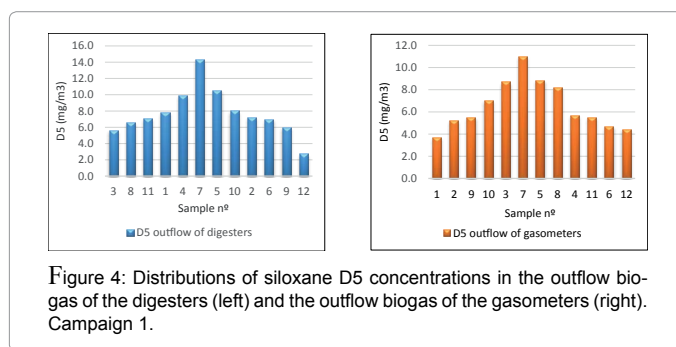
In campaign 2, the dose of FeCl<sub>3</sub> in the digestion was progressively reduced from the usual dose of 80 gr FeCl<sub>3</sub>/kg ms to zero. Table 2 shows the results for concentrations of siloxane D5 in the outflow biogas of the digesters and the outflow biogas of the gasometers, as well as the H<sub>2</sub>S concentration in the latter, obtained in the second campaign.

The results obtained from campaign 2 demonstrate the influence of the FeCl<sub>3</sub> dose on the D5 content in the biogas, since, as the FeCl<sub>3</sub> dose decreases, the concentration of D5 in the biogas rises and, at the same time, the concentration of H<sub>2</sub>S also increases, as shown in Figure 5. It should be noted that this increase in the concentration of S<sub>2</sub>H could lead to adverse effects in human health and the environment.

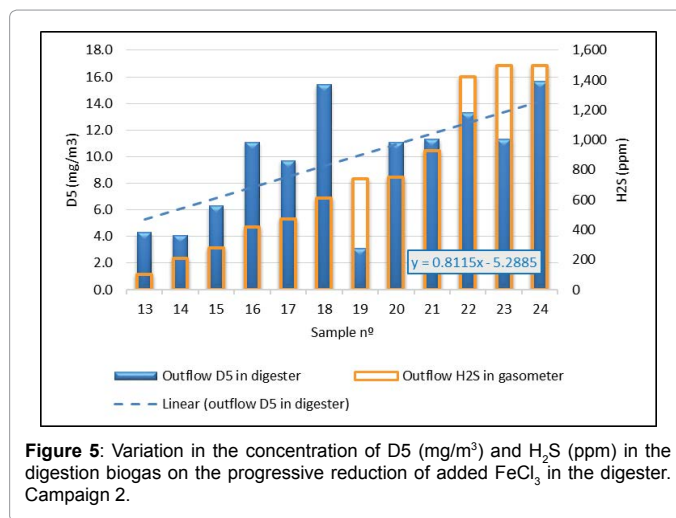
In the initial sampling campaign (campaign 1), the concentration of H<sub>2</sub>S in the biogas was at all times lower than 140 ppm. In the second campaign, as from the second sample (nº 14), it rose rapidly until it reached 1,500 ppm. At the same time, the concentration of D5 also increased, rising to values of the order of 10 mg/m<sup>3</sup> as from sample nº 16, except in sample nº 19, which can be considered an anomaly.



**Figure 3:** Percentage distribution of siloxane concentrations in the outflow biogas of the digesters (left) and the outflow biogas of the gasometers (right). Campaign 1.



**Figure 4:** Distributions of siloxane D5 concentrations in the outflow biogas of the digesters (left) and the outflow biogas of the gasometers (right). Campaign 1.



**Figure 5:** Variation in the concentration of D5 (mg/m<sup>3</sup>) and H<sub>2</sub>S (ppm) in the digestion biogas on the progressive reduction of added FeCl<sub>3</sub> in the digester. Campaign 2.

Despite this discordant value, the trend line of the D5 concentration in the biogas is clearly upwards (with a slope:  $m = 0.8115$ ), as the dose of FeCl<sub>3</sub> in the digester diminishes.

In campaign 2, the results obtained also reflect a reduction in D5 concentration between the outflow of the digester and the outflow of the gasometers, in this case of 14.4%, on average, a percentage similar to that seen in campaign 1.

No FeCl<sub>3</sub> dose was added at any time in campaign 3. Table 3 shows the results for D5 concentrations in this campaign, in which the H<sub>2</sub>S concentrations exceeded the measuring range of our equipment (>1,500 ppm). In this campaign, the mean concentration of siloxane D5 in the outflow biogas of the digesters was 14.5 mg/m<sup>3</sup>, with a minimum value of 7.6 mg/m<sup>3</sup> and a maximum of 19.1 mg/m<sup>3</sup>. The mean

concentration of siloxane D5 in the outflow of the gasometers was 11.7 mg/m<sup>3</sup>, with a minimum value of 5.8 mg/m<sup>3</sup> and a maximum of 19.4 mg/m<sup>3</sup>. In this case, the reduction of the mean concentration of D5 between the outflow of the digester and the outflow of the gasometers was, on average, 19.3%, a slightly higher figure than in the two previous campaigns.

Figure 6 shows the evolution of D5 concentrations (mg/m<sup>3</sup>) in the outflow biogas of the digesters (with no addition of FeCl<sub>3</sub>) and in the outflow biogas of the gasometers.

It can be seen that, in this case, with no addition of FeCl<sub>3</sub>, the trend line is much less pronounced (slope:  $m = 0.5741$ ) than in the previous case (slope:  $m = 0.8115$ ), in which the dose of FeCl<sub>3</sub> was progressively reduced.

The influence of the FeCl<sub>3</sub> dose on the presence of siloxanes in the biogas is therefore clear. The addition of FeCl<sub>3</sub> in the digesters for desulfurization also produces a significant reduction in the siloxane content of the biogas. In our case, with the (appropriate) dose of 80 gr FeCl<sub>3</sub>/kg ms, the mean value of the concentration of siloxane D5 in the outflow of the digesters was 7.7 mg/m<sup>3</sup>, with a variation range of 2.7 mg/m<sup>3</sup> (minimum) to 14.3 mg/m<sup>3</sup> (maximum), while, without any dose of the reagent, the mean concentration was 14.5 mg/m<sup>3</sup>, with a variation range of 7.6 mg/m<sup>3</sup> (minimum) to 19.1 mg/m<sup>3</sup> (maximum). With respect to the mean values, the reduction in the concentration of siloxane D5 on adding the appropriate dose of FeCl<sub>3</sub> in the digester was of the order of 47%.

These results agree with those obtained in other research on the elimination of siloxanes with iron compounds. Schweigkofler and Niessner [15] found percentages of siloxane elimination from WWTP biogas filtered through iron oxide towers of between 30% and 70%.

The percentage elimination of siloxanes from condensates resulting from the compression of the biogas in the gasometers was 17%, on average, a higher percentage than that reported by ConzeptGmbH [4] and Reina [9], who quantified it at around 10%.

Tables 4 and 5 offer a summary of the D5 concentrations in the outflow biogas of the digesters and in the outflow biogas of the less pressurized gasometers, respectively, obtained in the three sampling campaigns.

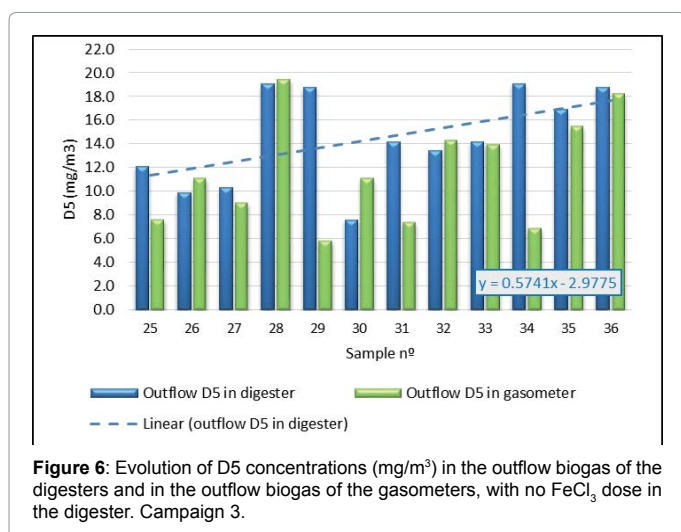


Figure 6: Evolution of D5 concentrations (mg/m<sup>3</sup>) in the outflow biogas of the digesters and in the outflow biogas of the gasometers, with no FeCl<sub>3</sub> dose in the digester. Campaign 3.

Campaign	Minimum concentration (mg/m <sup>3</sup> )	Maximum concentration (mg/m <sup>3</sup> )	Mean concentration (mg/m <sup>3</sup> )	Observations
1	2.7	14.3	7.7	Appropriate dose of FeCl <sub>3</sub>
2	3.1	15.7	9.7	Decreasing dose of FeCl <sub>3</sub>
3	7.6	19.1	14.5	No dose of FeCl <sub>3</sub>
Mean			10.6	

Table 4: Concentrations of D5 in the outflow biogas of the digesters over the three sampling campaigns.

Campaign	Minimum concentration (mg/m <sup>3</sup> )	Maximum concentration (mg/m <sup>3</sup> )	Mean concentration (mg/m <sup>3</sup> )
1	3.7	11.0	6.5
2	3.9	14.0	8.3
3	5.8	19.4	11.7
Mean			8.8

Table 5: Concentrations of D5 in the outflow biogas of the gasometers over the three sampling campaigns.

## Conclusions

No linear siloxanes were detected in any of the samples analyzed, while cyclic siloxanes were detected in compounds D4, D5 and D6, although at very different frequencies and concentrations.

In the outflow biogas of the digesters, siloxane D6 appeared in 33.3% of the samples, D4 in 75% and D5 in 100%. With respect to mean values, D4 represented 17% of the total siloxane concentration; D5 represented 81.9% and D6, 1.1%. In the outflow biogas of the pressurized gasometers, siloxane D6 was found in 16.7% of the samples, D4 in 33.3% and D5 in 100%. With respect to mean values, D4 represented 8.3% of the total siloxane concentration; D5 represented 90.3% and D6, 1.4%.

It can therefore be concluded that compound D5 appeared in all of the samples analyzed and that it is the compound which contributes most to the total concentration of siloxanes, both in the outflow biogas of the digesters (approximately 80%) and in the outflow biogas of the pressurized gasometers (approximately 90%).

The compression of the biogas, with the elimination of condensates, produces significant reductions in siloxane concentrations. In the specific case of D5, this reduction was of the order of 17%, on average.

The addition of iron chloride in the digesters for desulfurization also produces a significant reduction in the siloxane content of the biogas, and the greater the amount of iron chloride added to the system, the greater the reduction in siloxane concentration. In this case, for siloxane D5, the reduction was of the order of 47%, on average.

As a final conclusion, it can be said that there are not too many researches on the presence of siloxanes in the biogas generated in the anaerobic digestion of sludge from WWTPs, so we encourage readers to address this issue in their future research.

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