Universitat de Girona

Facultat de Ciències

Start-up of a lab-scale biotrickling filter for octamethylcyclotetrasiloxane (D4) removal from biogas

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Abstract

The biogas generated during anaerobic digestion in wastewater treatment plants and landfills is considered as a resource of renewable energy. Whereas its use not only contributes to reducing greenhouse gas emissions but also obtaining heat and electricity, biogas contains trace undesired compounds such as H_2S, volatile organic compounds and siloxanes among others. Volatile methyl siloxanes present in biogas cause the formation of silicate deposits during combustion affecting the efficiency of energy recovery systems.

The most widespread technology commercially available for siloxanes removal is adsorption onto porous materials, though their regeneration or replacement once exhausted is energy-consuming and expensive. On the contrary, biodegradation technologies may (i) reduce investment and operating costs, (ii) increment treatment capacities and (iii) require low energy and chemicals. It needs to be highlighted that siloxanes challenge biotechnologies due to their low solubility into water, which hinders their gas-liquid mass transfer and subsequently the liquid-biofilm transfer.

Within the present work, an aerobic biotrickling filter was operated for 56 days for the treatment of an air stream contaminated with octamethylcyclotetrasiloxane. At the beginning, D4 stripping from the laboratory-grown inoculum was observed and confirmed by cutting the siloxane entrance of D4. Even at high gas flows, D4 concentration of around 10 mg m^{-3} were observed. After inoculating with activated sludge from a wastewater treatment plant, the performance of the reactor showed 10% removal efficiencies at an empty bed contact time of 10 min. Moreover, decreasing the medium recirculation flow down to 15 mL min^{-1}, higher REs up to 21% were observed. Although being a pretty high gas residence time, low removal efficiencies were obtained due to the low solubility of D4 which leads to a low mass transfer to the liquid phase and consequently to the biomass.

Resum

El biogàs generat durant la digestió anaeròbica dins les plantes de tractament d'aigües residuals i abocadors és considerat com un recurs d'energia renovable. Mentre que el seu ús no només contribueix a reduir les emissions de gas d'efecte hivernacle, també se'n pot obtenir calor i electricitat. El biogàs conté compostos no desitjats com H_2S, compostos orgànics volàtils i siloxans, entre altres. Els Metil Siloxans Volàtils (MSVs) presents en el biogàs causen la formació de dipòsits de silicat durant la combustió que afecta a l'eficiència dels sistemes de recuperació d'energia.

La tecnologia disponible més estesa comercialment per l'extracció de siloxans és l'adsorció amb materials porosos, tot i que la seva regeneració o substitució una vegada que és esgotat consumeix energia i és car. Al contrari, les tecnologies de biodegradació poden (i) reduir la inversió i els costos operatius, (ii) incrementar les capacitats de tractament i (iii) no requereixen substàncies químiques i poca energia. És necessari destacar que les biotecnologies per eliminar siloxans són un repte a causa de la seva baixa solubilitat en aigua, el qual obstaculitza la seva transferència de massa a la fase líquida i subsegüentment a la seva transferència al biofilm.

Dins el present estudi, s'ha operat 56 dies un filtre percolador de biomassa pel tractament d'un corrent d'aire contaminat amb octametilciclotetrasiloxà. Al començament, "l'stripping" degut al creixement de les soques en plaques de cultiu amb concentracions de D4, va ser confirmat tallant la concentració de siloxà a l'entrada del reactor. Fins i tot a cabals de gas alts, la concentració de D4 observada continuava amb valors al voltant de 10 mg m^{-3}. Després d'inocular amb fang actiu d'una planta de tractament d'aigües residuals, el rendiment del reactor va mostrar 10% d'eficiència d'eliminació a un temps de contacte de llit buit de 10 min. A més, disminuint el flux de recirculació del medi a 15 mL min^{-1}, es van obtenir valors més alts d'eliminació, al voltant del 21%. Tot i que sent un gas amb un alt temps de residència, s'han obtingut eficiències d'eliminació baixes a causa de la baixa solubilitat del D4 que implica una baixa transferència de massa a la fase líquida i consegüentment a la biomassa.

Resumen

El biogás generado durante la digestión anaeróbica dentro de las plantas de tratamiento de aguas residuales y vertederos es considerado como un recurso de energía renovable. Mientras que su uso no sólo contribuye a reducir las emisiones de gas de efecto de invernadero sino también obtener calor y electricidad. El biogás contiene compuestos traza como H_2S, compuestos orgánicos volátiles y siloxanos, entre otros. Los Metilo Siloxanos Volátiles (MSVs) presentes dentro del biogás causan la formación de depósitos de silicato durante la combustión que afecta a la eficacia de los sistemas de recuperación de energía.

La tecnología disponible comercialmente para la eliminación de siloxanos es la adsorción con materiales porosos, aunque su regeneración o sustitución una vez que se agotado consume energía y es caro. Al contrario, las tecnologías de biodegradación pueden (i) reducir la inversión y los costes operativos, (ii) incrementar las capacidades de tratamiento y (iii) requieren sustancias químicas y poca energía. Es necesario destacar que las biotecnologías para eliminar siloxanos son un reto debido a la baja solubilidad en agua de los siloxanos, el cual obstaculiza su transferencia de masas a la fase líquida y por lo siguiente a su transferencia al biofilm.

En del presente estudio, se ha operado 56 días un filtro percolador de biomasa para el tratamiento de una corriente de aire contaminado con octamethylcyclotetrasiloxane. Al comienzo “el stripping”, debido al crecimiento de los socas en placas de cultivo con concentraciones de D4, fue confirmado cortando la concentración de siloxano a la entrada del reactor. Incluso a caudales de gas altos, la concentración de D4 observada continuaba con valores de alrededor 10 mg m^{-3}. Después de inocular con fango activo de una planta de tratamiento de aguas residuales, el rendimiento del reactor mostró un 10% de eficiencia de eliminación (RE) con un tiempo de contacto de cama vacío (EBCT) de 10 min. Además, disminuyendo el flujo de recirculación del medio líquido a 15 ml min^{-1}, se obtuvieron valores más altos de RE, alrededor de 21%. A pesar de que siendo un gas y utilizando un alto tiempo de residencia, se han obtenido eficiencias de eliminación bajas debido a la baja solubilidad del D4 que implica una baja transferencia de masas a la fase líquida y consiguientemente a la biomasa.

1. Introduction

In order to understand the purpose of the study that we are dealing with, we have to comprehend the processes that participated on the formation of biogas and the parameters that control the process and its efficiency.

The formation of biogas is an opportunity for the utilization of its components, like methane, for power production instead of the traditional power generation based on fossil fuels. Biogas is an attractive renewable fuel that can be used as prime matter for cogeneration plants, internal combustion engines and fuel cells (Li *et al.,* 2014).

Its use for energy production is justified by the high concentration of methane, around 40-70 %vol, and encouraged by several regulations aiming at the reduction of greenhouse gas (Accettola *et al.,* 2008). Biogas has become a notable alternative to conventional fuels in the production of electricity and heat (De Arespacochaga *et al.,* 2015).

1.1. Biogas formation and composition

Besides methane, anaerobic digestion also produces other subproducts like CO_2 (30-50 %vol), a lower percentage of N_2, H_2, CO and other trace compounds. Methane and carbon dioxide are greenhouse gases, and therefore cannot be discharged to the atmosphere. Due to the high calorific value of methane for its energy and heat exploitation by the combustion, we can reduce the greenhouse gases emissions. However, exploitation of biogas is usually limited by the harmful trace constituents like hydrogen sulphide, halides and silicon-containing compounds also referred as volatile methyl siloxanes (VMSs) (Accettola *et al.,* 2008).

The biogas is a byproduct from the anaerobic digestion of the organic fraction of municipal solid wastes, livestock residues or organic agroinsudtrial waste (Muñoz *et al.,* 2015). In any case all types of biomass can be used as substrates for biogas production but its composition and the methane yield depends on the nature of the raw materials and the operational conditions used during anaerobic digestion, that determine the chemical composition of the biogas (Ryckebosch *et al.,* 2011).

The main processes that take place in anaerobic fermentation (summarized in Figure 1) are:

- Hydrolysis. This first phase consists in the hydrolysis of particles and complex molecules such as proteins and lipids which are primarily hydrolysed by extracellular, hydrolases, excreted by microbes present in Stage 1 (in Figure 1) generating soluble compounds like amino acids, fatty acids…

- Acetogenesis. The acetogens bacterial species synthetize acetate from carbon dioxide and hydrogen gas.

- Methanogenesis. Finally, this is the last stage of the process where acetic acid, H_2 and CO_2 are transformed by methanogenic bacteria to forms methane (CH_4), carbon dioxide (CO_2), water and other byproducts.

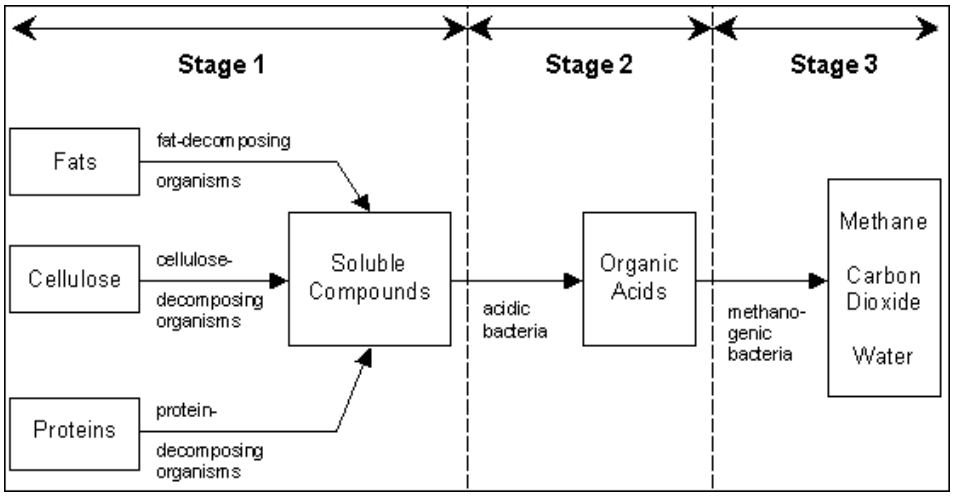

Figure 1. Anaerobic fermentation stages and implicated bacteria communities (Dewil et al. 2006).

Biogas is generally produced in landfills, methanation plants and wastewater treatment plants (WWTP). In the latter case, how we had said, the production of biogas purification, imply risk due to the presence of harmful compounds such as siloxane by the fact that since in recent years the use of silicone and siloxane, from cosmetics, detergents…, has increased their concentration in wastewater (Bletsou *et al.,* 2013).

Due to the presence of these compounds, the energetic utilization of biogas is severely compromised by its volatile organic silicon compound content (De Arespacochaga *et al.,* 2015).

The necessity of searching ways to degrade and eliminate methyl siloxanes arise on the silicone oxide that deposits in biogas combustion engines and valves, causing their abrasion, overheating and malfunctioning (Muñoz *et al.,* 2015).

1.2. Characteristics of methyl siloxanes

The siloxane are organosilicon chemical compounds present in biogas that could not be decomposed in the process of a sludge treatment plant (Dewil *et al.,* 2006). These siloxane are used in several industrial and domestic applications, including as antifoaming agent, in care products as coatings and in cosmetics and personal care products (De Arespacochaga *et al.,* 2015).

The most volatile siloxanes, such as hexamethyldisiloxane (D2), disperse into the atmosphere and react with OH radicals to form OH-substituted silanediols. On the other hand, compounds such as octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) remain in wastewaters due its low water solubility (Cabrera-Codony *et al.,* 2014). Therefore they are not accumulated on water phase but remains

on the sludge flocks that are used to produce biogas and due its high volatility remains in the gas phase where biogas is produced (De Arespacochaga *et al.,* 2015).

In Table 1 shows some characteristics that siloxanes present.

Table 1. Selected physic-chemical properties of VMSs commonly found in biogas.

Chemical name	Abbreviation	Chemical formula	Molecular weight (g mol^{-1})	Boiling point (ºC)	Solubility (mg L^{-1} at 25 ºC)
Hexamethyldysiloxane	L2	$C_6H_{18}OSi_2$	162	107	0.93
Octamethyltrisiloxane	L3	$C_8H_{24}O_2Si_3$	237	153	0.034
Hexamethylcyclotrisiloxane	D3	$C_6H_{18}O_3Si_3$	223	135	1.56
Octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	297	176	0.056
Decamethylcyclopentasiloxane	D5	$C_{10}H_{30}O_5Si_5$	371	211	0.017

The organosilicon compounds are oxidized during biogas combustion into microcrystalline silicon dioxide (De Arespacochaga *et al.,* 2015), a residue with chemical and physical properties similar to glass during the combustion. Silicon dioxide deposits on valves, cylinder walls, cause abrasion and blockage of pistons, cylinder heads and valves.

The reason for that are not eliminated the siloxane during anaerobic sludge digestion is by the temperature fact. When the temperature is approximately 60 °C, the volatile siloxane is running as part of biogas because this compounds are extremely volatile.

The type of siloxane that we take into account are Volatile Methyl Siloxanes (VMSs) because they are detected in biogas after anaerobic digestion, due to its low molecular weight. They are chemically and physically inert, resistant to oxidation and to high temperatures, have low surface tensions, water repellence and high compressibility (De Arespacochaga *et al.,* 2015). Therefore, in volatile siloxane are different types depending on their structure. Its structure can be linear or cyclic as shown in Figure 2, and the unlike between the different linear and cyclic structures are the number of dimetylsiloxanes and silica atom (Dewil *et al.,* 2006).

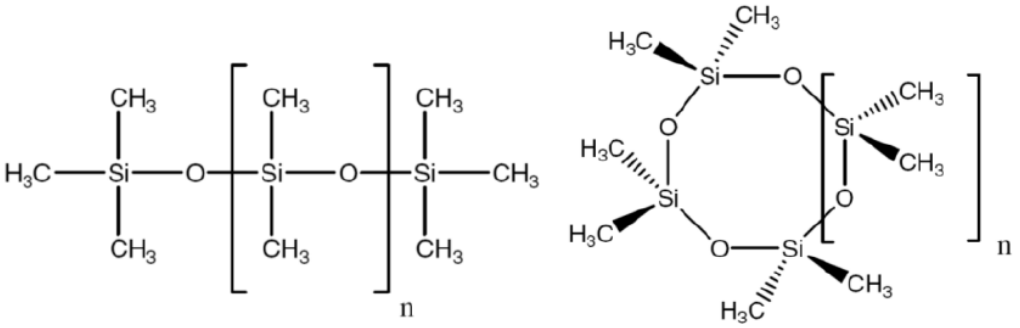

Figure 2. Linear and cyclic siloxane structure, w*hen n=1, the left siloxane is L3 and the right siloxane is D4*

Basically the main problem that we are focus on is on the elimination of siloxanes on biogas for its utilization as power source because of its accumulation in internal combustion engines for combined heat and power generation (Muñoz *et al.,* 2015), usually causing an erosion of the turbine blades and subsequently decreasing the operating efficiency (Ajhar *et al.,* 2010).

In resume the consequence of siloxane are the abrasion of the pieces of the engine or the accumulation of layers that inhibit heat conduction that can lead to increased emissions of CO and formaldehyde.

1.3. State-of-the-art on siloxane removal

1.3.1. Physical and chemical technologies

The most used technology to reduce volatile methyl siloxanes presence is adsorption onto activated carbon (Ajhar *et al.,* 2010) which is actually the only technology commercially available for siloxane removal (Muñoz *et al.,* 2015). Non-regenerative adsorption on fixed beds of activated carbon or graphite is the most common concept (Ajhar *et al.,* 2010) where biogas is conducted through an adsorbing filter for its purification.

Adsorption onto activated carbon has shown siloxane removal efficiencies up to 95% when dry biomethane is treated. However, it has been observed how the humidity in biogas may reduce the adsorption potential of the AC (Ryckebosch *et al.,* 2011).

Others adsorbents such as silica gel (Sigot *et al.,* 2014) and zeolites (Cabrera-Codony *et al., 2017)* have shown great performances in siloxane removal with efficiencies up to 99%.

Absorption is the second major unit operation which has been applied to siloxane removal (Ajhar *et al.,* 2010). This removal technology consists on conducing the biogas air flow into an absorbent liquid where siloxanes get trapped.

Siloxane absorption into organic solvents such as tetradecane or Selexol (Schweigkofler & Niessner 2001) in spray or packed bed towers can provide siloxane removal efficiencies of 97-99%. Figure 2 presents a schematic of the experimental experiment.

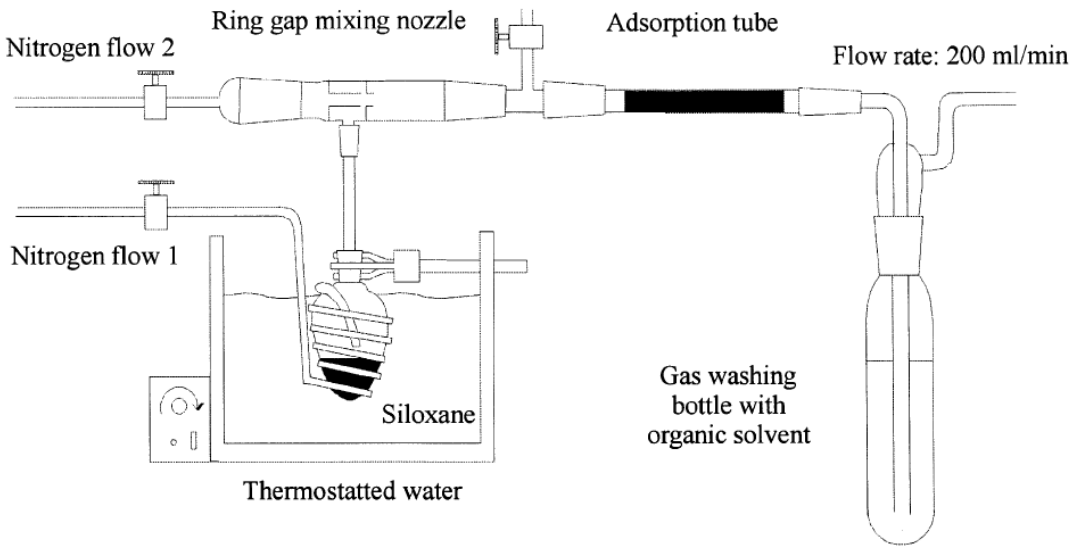

Figure 3. *Experimental set-up for absorption experiments* (Schweigkofler & Niessner 2001).

These physical and chemical technologies presents the principal advantage of great removal efficiencies. However, the high operating costs related to the regeneration of the adsorbents for its physical removal, and also the high volume of absorbent utilized for its chemical removal makes these technologies economically not viable or highly expensive to maintain (Muñoz *et al.,* 2015).

1.3.2. Biological technologies

A low number of researchers have studied the D4 biodegradation process for removal of D4 from biogas and reported to be relatively biodegradable with some encouraging results. Due to the low water solubility of siloxanes, biodegradation is limited due to the low mass transfer from gas to liquid phase, and therefore siloxanes availability for biomass.

Table 1 presents the different operating conditions and removals efficiencies of the published studies.

In Accettola *et al.,* (2008) study worked with D3 siloxane setting up a lab-scale biotrickling filter packed with inert Pall Rings inoculated with batch culture and had removals efficiencies of 10% with an inlet concentration of 45 mgD3·m^{-3} and gas flow rate of 0,9 L min^{-1}. Moreover in a next step the gas flow rate of the biotrickling filter was fixed on 0,7 L min^{-1} which led to a concentration of 59 mg D3 $m^{-3}$and also done 10% of removal efficiency. Results show that octamethylcyclotetrasiloxane can be biodegraded by *Pseudomonas* group bacteria with an ERBT of 3.5 min.

Table 1. Reactor operation conditions of several studies compared with own study.

Ref.	Comp.	Inlet Conc. (mg m^{-3})	Volume (L)	Gas flow (ml min^{-1})	Liquid flow (ml min^{-1})	Gas/liquid ratio	EBCT (min)	RE (%)
Popat & Deshusses (2008)	D4	45	0.39	500	3.5	142.9	5-20	10-60
Accettola *et al.*, (2008)	D3	45-77	1.92	500-900	250	2-3.6	3-4.2	10-20
Wang *et al.*, (2014)	D4	10-150	1.96	65-130	166	0.39-0.78	15-30	58-60
Li *et al.,* (2014)	D4	20-140	0.44	333-1333	333	1-4.01	3.3-13.2	3-60
Soreanu (2016)	D4 D5	15-37 (D4) 25-47 (D5)	6.70	84-184	500	11/22	36.5-80.4	8-60

The siloxane elimination was also tested (with D4 inlet) in a lab scale reactor by Popat and Deshusses (2008). A 15% removal efficiency of D4 was reached at a residence time of 4 min comparable to that of 10 - 20% reported by Anccettola *et al.,* (2008), with an air flow rate of 0.5 L min^{-1} and a resulted concentration of 45 mg D4 m^{-3}. As the EBRT was increased significantly (longer contact time for D4 into BTF) the RE raised too linearly with a maximum removal of 43% at an EBRT of 19.5 min (Popat & Deshusses 2008).

On Wang *et al.,* (2014) study to investigate the removal efficiency of D4, a BTF was set up as shown in Figure 4. The packing material in the BTF was polypropylene cascade rings of 4-6 mm and its height was 100 cm and obtained the several numbers of RE eliminations.

Li *et al.,* (2014) study developed a lab scale aerobic biotrickling filter. BTF with a packaging height of 1000 mm and filled with irregular-grain lava rocks of 8-10 mm particle diameter, exhibited highs removals efficiencies (74 %) at EBCT of 13.2 min.

With an inlet concentration of 50 mgD4 m^{-3} the RE achieved the maximum value 60.2 % and EBRT 24 min. With a higher inlet concentration the RE obtained were low. Its results were higher compared with previous studies because of the bacterial strain was originated from an activated sludge containing organic silicon compounds (Wang *et al.,* 2014).

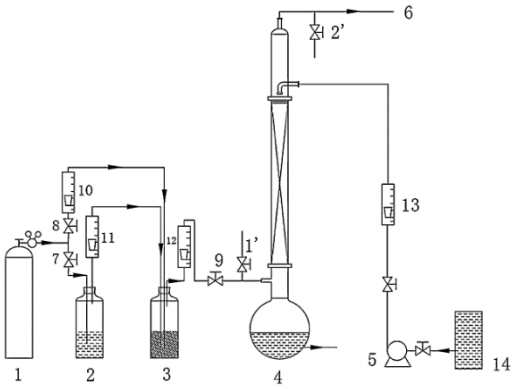

Figure 4. The schematic of the experimental setup. (1) Air cylinder; (2) D4 bottle; (3) Mixer>; (4) BTF; (5) Booster pump; (6) Emptying; (7)-(9) Valve; (10)-(12) Gas flowmeter; (13) Liquid flowmeter; (14) Fresh mineral medium; (1') Inlet gas sampling; (2') Outlet gas sampling (Wang *et al.,* 2014).

Finally, it was tested D4 and D5 removal from biogas, with a maximum performance removal of approximately 60 %. Despite high EBRT (high bed contact time) the RE obtained indicate that BTF was mass-transfer limited (Soreanu 2016).

In resume, the stage of the research on biodegradation removal of siloxanes is basic and with low removals efficiencies (around 10 %) and on previously researches shows high RE with great EBRT. These highs removals at highs EBRTs indicate a low viability to do it an industrial scale.

1.4. Ethics and sustainability criteria

This work aimed to study the biological degradation of D4 siloxane to present a cost-effective technology with less greenhouse gas emissions than others alternatives like chemical and physical technologies. The relevance of the project is to resolve the damages caused by the siloxanes in combustion engines and take benefit of the energy produced by the biogas combustion. More than ever, biogas utilization becomes a relevant power source because the necessity to reduce global warming and fossil fuel utilization.

The sampling methodology followed in the study, as well as the analytical methods used, followed different sustainability criteria like reducing the solvent utilized for minimizing the residues generated and its subsequent external treatment or using an air inlet gas flow to the BTF in front of a pure oxygen inlet gas. In order to reduce the waste generated we also recycled the vials and septum taps, previously cleaned and subjected to heat for volatilizing the siloxanes.

With regard to professional ethics the study had not made bad scientific practises, like plagiarism or invented data, in order to maintain the ethics of the work and our self-morality.

It is important to follow a minimum standards on ethical and sustainability in order to reduce the volume of waste and chemicals used it this study.

2. Objectives

The principal object of this study is the removal of volatile siloxanes present in biogas from wastewater treatment plants through biological treatment in order to increase the quality of biogas and avoid possible problems in burning engines.

We purpose to understand the biodegradability of the methyl siloxanes compounds that are present in the biogas produced during the anaerobic digestion. So, the objectives of the present work are the following.

- Start-up of a lab-scale aerobic biotrickling filter for the treatment of synthetic gas contaminated with siloxanes.

- Investigate the siloxane removal performance in the BTF packed with lava rock and inoculated with biomass from a WWTP sludge.

- Evaluate the effect of the empty bed contact time and other parameters such as liquid flow rate, in the performance of the BTF.

3. Materials and methods

3.1. Microorganism and cultivation medium

The first inoculums utilized for the reactor were prepared by the Department of Microbiology and they consisted in cultivation of different bacterial strains, found to be capable of growing with the presence of siloxanes in agar plates. After some weeks, when growth of the communities was evident, they were used for inoculating the BTF reactor.

The second set of microorganisms used in the present study were obtained from activated sludge collected from the secondary treatment reactor in the wastewater treatment plant of Rubi (Barcelona), see Figure 5. This treatment plant was chosen due to the high presence of siloxanes in the influent of the WWTP, fact that might be explained because of a silicon company located near the wastewater treatment plant.

Since high concentrations of siloxanes were monitored in the influent of the plant, it was assumed that the biomass in the biological reactor would be more adapted to degrade this kind of pollutants.

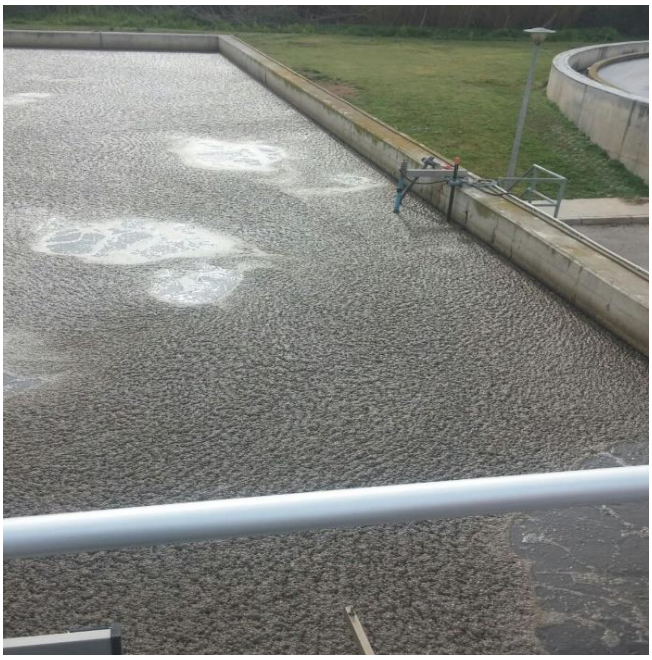

Figure 5. Secondary treatment tank where we sample the sludge.

The sludge from the supernatant of the biological reactor of the WWTP was directly collected and conserved in a portable fridge. Before incorporating it into the biotrickling filter, we let sediment the biomass and decanter the water present on the sample with the finality of concentrate more the biomass. Moreover, we added water several times to the sample to clean the organic matter and concentrate the sample.

For the determination of Total Suspended Solids (TSS – Eq. 1), firstly filters were put in the oven at 105 ºC for an hour before being weighted (A - tare). 10 mL of sludge was filtered by connecting a büchner flask to a vacuum pump. Filters were placed in the oven at 105 ºC for 24 hours, in the desiccator for 10 min and then weighted again (B).

Secondly, these same filters were placed in the muffle at 550 ºC for 1 hour, dessicator 10 min and weighted (C) for the determination of the Volatile Suspended Solids (VSS – Eq. 2).

$$\text{Eq. 1;} \quad TSS\left(\frac{mg}{L}\right) = \frac{(A-B)\cdot 1000}{V_{sample}\,(ml)} \qquad \text{Eq. 2;} \quad VSS\left(\frac{mg}{L}\right) = \frac{(C-B)\cdot 1000}{V_{sample}\,(ml)}$$

The mineral medium provided for the growth of microorganisms are shown on Table 2. The pH of the medium was adjusted to 6,97 with NaOH and complemented with 0,5 ml of micronutrients SL-10 x2 and 1 ml of vitamin 10 mix x10.

Table 2. Mineral medium composition.

Components	**Concentration (g L^{-1})**
NaCl	0.5
$MgSO_4 \cdot 7H_2O$	0.1
$CaCl_2$	0.01
NH_4Cl	0.02
$NaNO_3$	1.0
$KH_2PO_4 \cdot H_2O$	0.58
HEPES 10 mM	2.38

The mineral medium was replaced twice a week to ensure that the microorganisms had the vitamin source to grow. Every time about 250 mL of the old medium was replaced by new mineral medium.

3.2. Biotrickling filter system

The glass column filter was packed with lava rock (7-12 mm particle size) and the bed height was 36 cm and 6 cm of diameter. The Figure 6 shows the schematic diagram of biotrickling filter setup studied within this work.

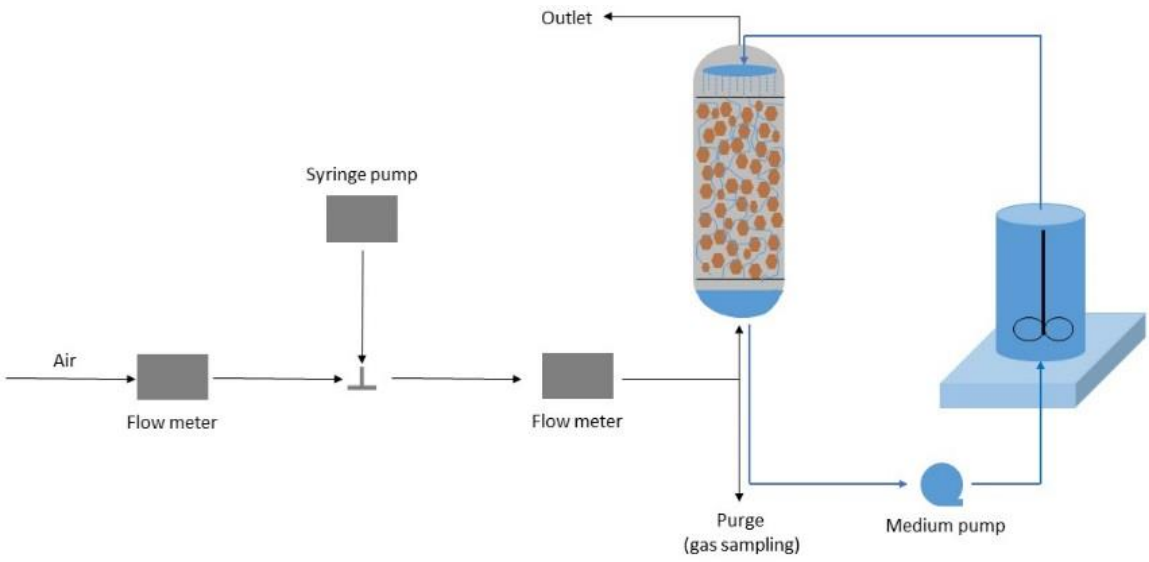

Figure 6. Schematic of biotrickling filter system. In black (gas line) and in blue (liquid line).

The mineral medium was recirculated from the bottom to the top of the column by a peristaltic pump (Watson Marlow) at a flow of 35 ml min^{-1} to provide the bacteria the moisture, minerals and vitamin necessary for growth.

A synthetic gas stream contaminated with D4 was generated by injecting, by means of a syringe pump (Harvard Apparatus), a infuse rate flow of 0,7845 µl h^{-1} of pure D4 (Sigma Aldrich, 98%) to an air flow of 500 mL min^{-1} regulated by a mass flow controller (Alicat), in order to obtain an inlet D4 concentration of 50 mg m^{-3}.

Since the syringe capacity was 250 µl, D4 had to be refilled every 6 days. Then, 100 mL min^{-1} were sent to the BTF inlet so the empty bed contact time was of 10 min. in the beginning of the operation.

The flux direction of the mixing gas was in countercorrent flux of the mineral medium, so the mixing gas was circulated from the bottom of the column to the high of the system.

Finally, the performance of the system was estimated by calculating the elimination capacity of D4, where Q_0 is influent flow, $D4_0$ is D4 concentration at inlet, Q_1 is outlet flow and $D4_1$ is D4 concentration at outlet (Eq. 3).

Eq. 3; $$Elimination\ \% = \frac{Q_0[D4_0] - Q_1[D4_1]}{Q_0[D4_0]} \cdot 100$$

3.4. Analytical and sampling procedures

3.4.1. Analytical methodology

A gas chromatographs were used in this work to D4 quantification; the main conditions of each one are described in Table 4.

Table 4. GC-MS method developed for D4 siloxane quantification.

Characteristics	#1 GC Agilent Tech. 5977E
Injection type	Split 1:6
Matrix	Gas
Column type	HP-5 ultra inert
T injector (ºC)	150
Sample volume	1 ml gas loop
D4 retention time (min)	5.3
D4 ions (m/z)	133, 207, 281

Firstly, D4 concentrations in the gas streams (inlet and outlet) of the biotrickling systems was measured using gas chromatograph #1, with a mass spectrometry detector (5977E series GC/MSD system, Agilent Technologies). On Figure 7 are shown the valve injection and the GC utilized.

The ramp temperature designed to D4 quantification consist in a 60ºC of initial temperature and 1 min of hold time. After that, the temperature raises at 20ºC min^{-1} to reach 150ºC. Finally, the temperature ups to 250ºC at 50ºC min^{-1}.

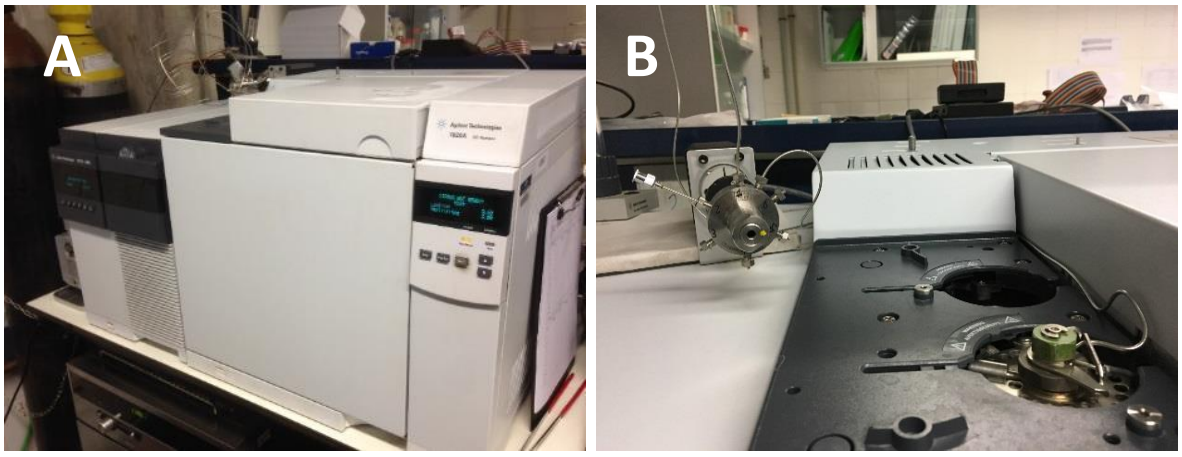

Figure 7. Pictures corresponding to (A) GC-MS and (B) valve injector used in the laboratory.

3.4.2. Sampling methods

In this project, we applied one methodology of sampling to adapt the sample to the requirements of the GC used.

On this study we had available a gases chromatograph with mases with manual puncture, so we sampled directly the mixing gas of the output and input of the biotrickling filter with a Tedlar gas bag (Figure 8) of 1 litre capacity with around 10 min of sampling. When the sample was into the Tedlar gas bag, we catch with a gas syringe 25 ml of this gas and putting it directly on the GC-mases.

Figure 8. Tedlar gas bag used on sampling methods.

4. Results and discussion

An aerobic BTF was started the 22nd of September 2016 until the 21st of December 2016 when the sinister of the laboratory occurred. The lab-scale BTF was operated during a total time of 56 days.

Results of the reactor monitoring have been divided in three periods in order to make an easier understanding. The concentration in the inlet and outlet, and the removal efficiency of D4 have been evaluated.

The conditions of each period are summarized in Table 5.

Table 5. Different conditions applied to the BTF.

Period	Days	Gas flow (mL min^{-1})	EBCT (min)	Liquid flow (mL min^{-1})
I	0 – 13	100	10	35
II	13 – 27	100	10	35
III	27 – 56	100 – 400	2.6 – 10	10 - 35

4.1 Operation of the biotrickling filter

4.1.1. Period I – Start-up of the reactor

Operation of the biotrickling filter (Period I, days 0 - 13) was started with a gas flow rate of 100 mL min^{-1}, an inlet D4 theoretical concentration of 50 mg m^{-3} and 36 cm of lava rock as packing bed height. The empty bed contact time in the reactor was of 10.3 min and medium recirculation flow was 35 ml min^{-1}.

The reactor was inoculated at the beginning with laboratory strains grown in agar dishes by the Microbiology department in order to biodegrade the presence of siloxane in the biotrickling column.

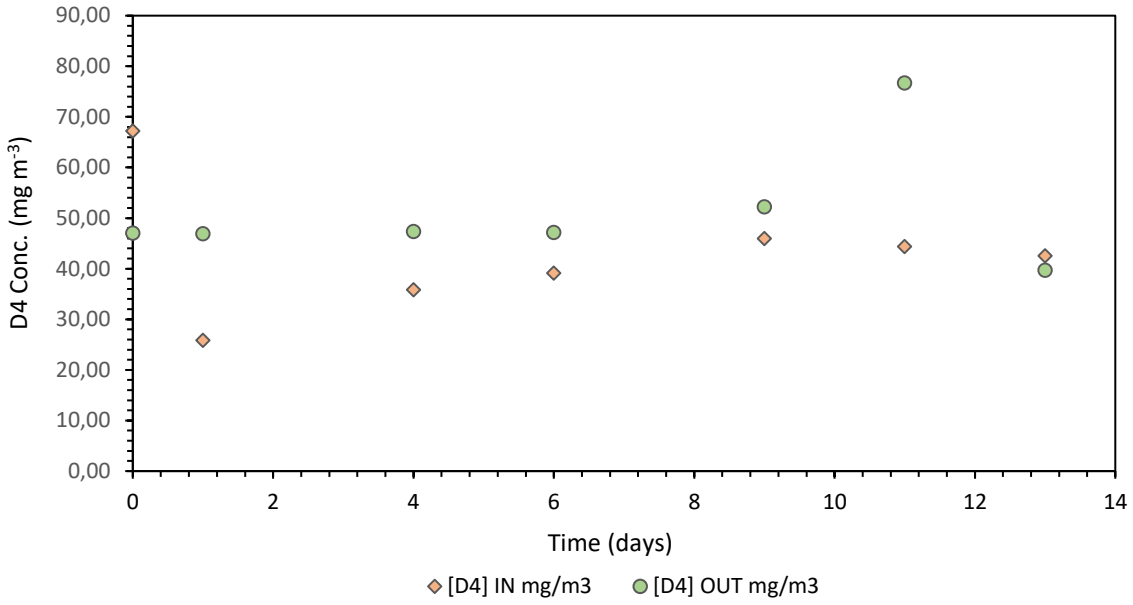

Figure 9. Results obtained of D4 inlet and outlet concentration in the days 0 – 13 of the study.

As shown in Figure 9, higher D4 concentration was found in the outlet than in the inlet of the reactor, which did not to seem to have any sense at the beginning. This repetitive fact could be attributed to a lower acclimation of the bacteria or a stripping phenomenon. The stripping was thought of coming from the inoculum prepared in the laboratory. Since inoculums were prepared by washing out bacteria grown from the agar plates, pure siloxanes used for bacteria's growth could have ended up being transferred to the inoculum disposed to the reactor. Then, by applying an air flow (inlet gas) to this inoculum, D4 was stripped out resulting in a higher concentration in the outlet of the reactor.

4.1.2. Period II – D4 stripping

In order to confirm this stripping phenomenon, during stage II (days 14 – 27) the syringe pump feeding the air flow with D4 was stopped.

As it can be observed in Figure 10, during this stage, there was no D4 in the inlet but concentrations of 10 - 25 mg m^{-3} were found in the outlet. Therefore, stripping phenomenon was confirmed.

Eventually, this incoherence was attributed to the stripping of D4 present in the inoculum prepared. Since bacteria was grown in agar plates, not only agar nutrients but also siloxanes were added, and by washing the communities, D4 was consequently being washed out to the inoculum.

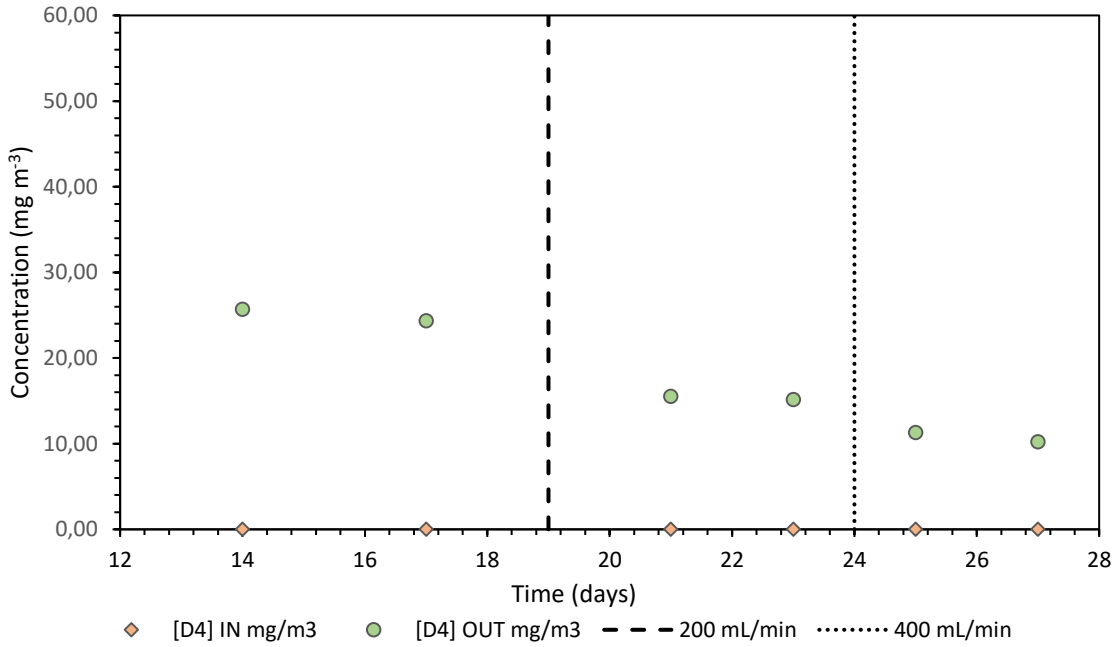

Figure 10. Results obtained of D4 inlet and outlet concentration at the days 13 – 27 of the experiment.

For further confirmation and stripping of all the D4 present in the reactor, we tried different flows of air (without D4 in the inlet). Table 6 shows the different conditions applied to the reactor.

Table 6. Different air flow rate to strip the BTF.

Days	Air flow rate (mL min^{-1})	EBCT (min)	D4 outlet conc. (mg m^{-3})
13 - 19	100	10.3	25
19 - 24	200	5.1	15.2
24 - 28	400	2.6	10.5

In the first stage (days 14 – 19), where the flow was 100 mL min^{-1} with an EBCT of 10.3 min, we obtained outlet concentration around 25 mg m^{-3}. When the flow rate was raised to 200 mL min^{-1} the outlet concentration of D4 decreased to 15.2 mg m^{-3}. Finally, in the last stage, the flow rate was increased to 400 mL min^{-1} obtaining an EBCT of 2.6 min. Results during this period showed that with such high flow the outlet concentration of D4 obtained was 10.5 mg m^{-3}.

Overall, we could observe that by increasing the inlet flow, D4 siloxane was stripped out faster.

4.1.3. Period III – BTF evaluation for D4 removal

After confirming the siloxane stripping, the syringe pump injecting D4 to the gas was restarted to give the same conditions as in the beginning of the study. Moreover, the bioreactor was inoculated with activated sludge from a WWTP to avoid stripping caused from the D4 on the culture plate of the laboratory strain.

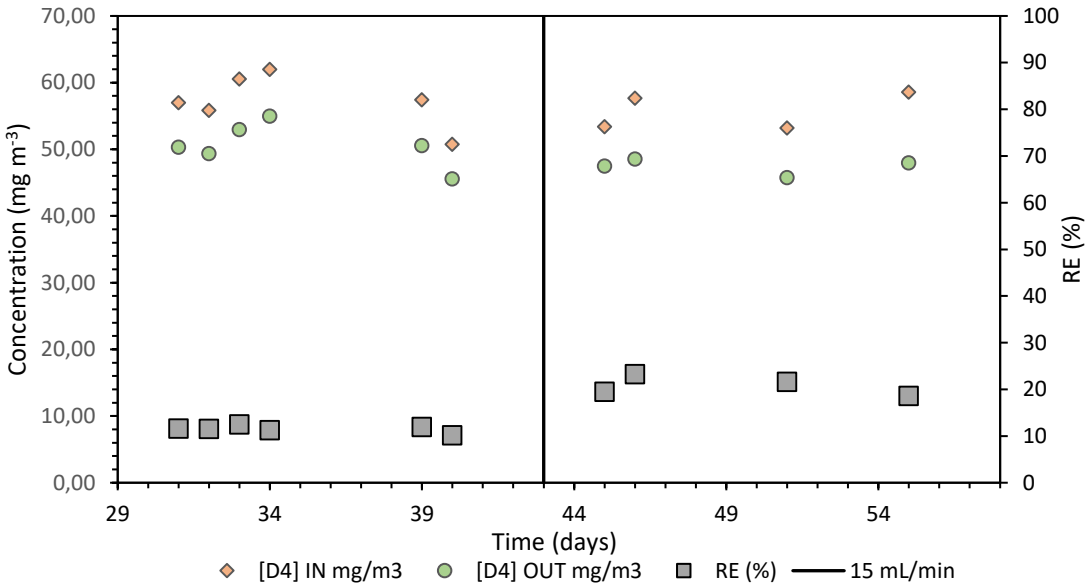

Figure 11. Results obtained of D4 inlet and outlet concentration at the days 30 – 56 of the experiment and the RE (%) of the BTF.

In this period, results obtained (shown in Figure 11) showed a positive removal efficiency ranging from 10 up to around 20%. Due to this reactor performance, a proper acclimation of the bacteria from WWTP sludge was accomplished. These results are comparable those obtained by Accettola *et al.*, (2008) or Popat and Deshusses (2008) with

This period was divided in two stages (summarized in Table 7), in which liquid recirculation flow was changed to study the effect of the water presence in the column of the reactor.

Table 7. Different operation parameters of the BTF between days 30 - 55.

Days	EBCT (min)	Liquid flow rate (mL min^{-1})	RE (%)
30 - 43	10.3	35	11.2
43 - 55	10.3	15	19.87

When liquid recirculation was decreased from 35 ml min^{-1} down to 15 mL min^{-1}, the removal efficiency increased more than an 8%, resulting in better performance of the reactor when less water was present in the column. Liquid flow was decreased to a more comparable flow to

Popat & Deshusses 2008, and results were in good agreement with their reactor's performamce, 17% RE at 8 min of gas residence time.

It is generally known that high vapour pressures and low water solubility (0.056 mg L^{-1}) are the principal characteristics of D4. These properties limit their solubility in the water phase and hinder the removal capacity of D4 in the BTF (Wang *et al.,* 2014).

Overall, the mass transfer of the compound from the gas into liquid phase is strongly limited as has been previously observed (Accettola *et al.,* 2008), and higher recirculation flows, leading to a higher water quantity in the reactor, would adversely affect the bioavailability of D4 siloxane to the biomass.

4.2. Test gas stability

After evaluating all the results of this study, it was observed that the D4 inlet concentration of the biotrickling filter did not show good stability. In order to improve this for a future stage, the influence of the infuse rate in the syringe pump and the gas flow were studied for obtaining a theoretical concentration of 50 mg m^{-3}, conditions shown in Table 8.

Table 8. *Different parameters stablished for testing the gas stability.*

	Infuse rate ($\mu L\ h^{-1}$)	**Air flow ($mL\ min^{-1}$)**
Condition 1	0.7845	250
Condition 2	1.5690	500

Results from the test of gas inlet stability were obtained by injecting the resulting test gas directly to the GC-MS. Results in Figure 12 show that by increasing the infuse rate to 1.5690 µL h^{-1} of D4 siloxane, the signal in the chromatograph is much more linear, thereby obtaining better stability.

The two conditions have in common the high variability of the GC signal at the beginning, when the pump was started. However, from 100 min on, signals start getting more stable. After this, the condition 2 with higher volume injection and gas flow demonstrated better performance. The relative error of condition 1 and 2 was 14.38 and 5.13 % respectively.

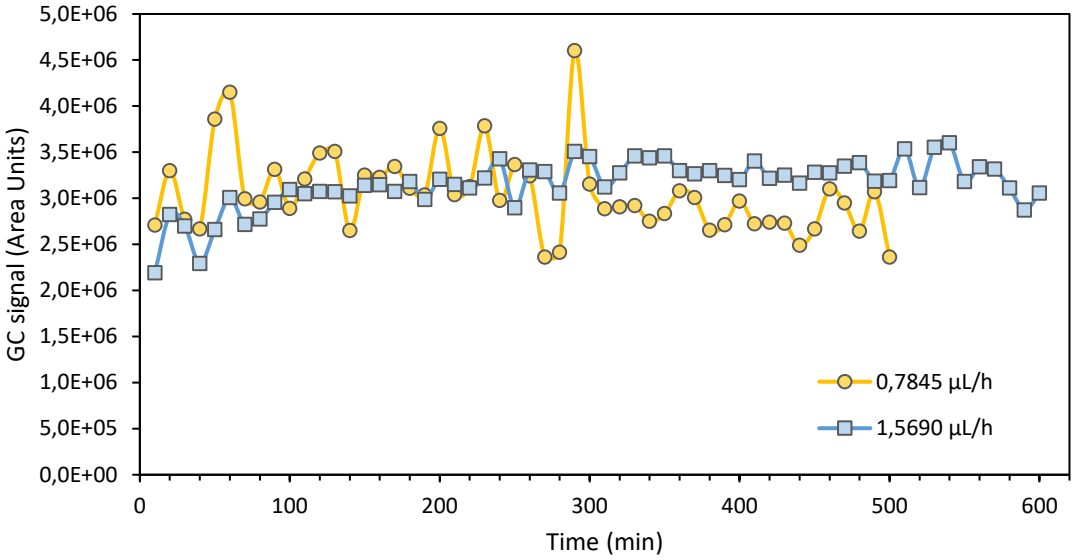

Figure 12. GC signal obtained of the test gas stability of the syringe pump.

Therefore, the next stage of the research would consist in fix the infuse rate at 1.5690 µL h^{-1} and gas flow rate of 500 mL min^{-1} so that the D4 concentration in the inlet would not have much variability.

5. Conclusions

D4 siloxane biodegradation has been investigated in order to evaluate the possibility of using a biofiltration system to treat synthetic air polluted with D4, to research a cost-effective and environmentally friendly alternative to the present technologies for avoiding damage of the equipment caused by siloxanes.

During the start-up of the biotrickling filter, which was inoculated with laboratory strains from the Microbiology department, octamethylcyclotetrasiloxane concentrations obtained were higher in the outlet. The possibility of a siloxane-stripping phenomenon was considered since communities grown were washed on agar plates (with siloxane presence) to prepare the inoculum. This hypothesis was confirmed in a second stage where the D4 inlet infusion was stopped and high concentrations of D4 at outlet were detected again. This fact confirmed the stripping of D4 in the reactor and the D4 provenance from the inoculum. Due to this unexpected event, the removal efficiency could not be monitored during this period of time, and consequently the biomass acclimation. It was concluded that for a better operation, inoculum had to be cleaned from any siloxane source.

The variability in the test gas generation was also investigated, by studying D4 infuse rate into the air stream. The stability of the resulting test gas showed to be influenced by the infuse rate in the syringe pump, and the gas flow. It was concluded that when increasing the infuse rate of D4 into a higher gas flow, the D4 signal in the GC-MS demonstrated more stable performance.

On the other hand, after reinoculating the reactor with activated sludge results showed a stable 10% of removal efficiency. That positive RE values suggested that the microbial consortium used for inoculation of the system had been acclimatized successfully. Moreover, the effect of decreasing the liquid flow recirculation was investigated in order to study the influence of the presence of water. The RE values increased to a significant 20%, suggesting that moisture presence in the reactor had negative effects to the transfer of the compound from the gas into the liquid phase due to the low solubility of D4. Consequently, it makes harder the biological degradation of D4 siloxane since water hinders its bioavailable to the microorganisms. Removal efficiencies comparable to the previous bibliography were obtained.

It needs to be highlighted that the present work aimed to further investigate the effect of others parameters such as the empty bed contact time. However, this study has been conditioned by the accident that took place in the laboratory the 24th of December. The lab-scale reactor was interrupted due to an electricity stop, and left the reactor without being fed for the week after. The next step of the research would be continuing the study with higher EBCT to see if RE values obtained are superiors with the major aim of develop a low-cost unit able to upgrade biogas by biological treatment system.

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