Universidad de Valladolid

Escuela de Doctorado Universidad de Valladolid

PROGRAMA DE DOCTORADO EN INGENIERÍA QUÍMICA Y AMBIENTAL

TESIS DOCTORAL:

INNOVATIVE BIOPROCESSES FOR SILOXANES REMOVAL FROM BIOGAS AND GASEOUS EMISSIONS

Presentada por **Celia Pascual Centeno** para optar al grado de
Doctor/a por la Universidad de Valladolid

Dirigida por:
Raquel Lebrero Fernández
Raúl Muñoz Torre
Sara Cantera Ruiz de Pellón

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Resumen

Hoy en día, problemas medioambientales como el cambio climático, la formación de ozono troposférico, la sobreexplotación de recursos naturales o la contaminación por emisiones gaseosas constituyen una de las mayores preocupaciones a nivel mundial. Las políticas y estrategias desarrolladas actualmente, como el Pacto Verde Europeo, se centran en impulsar el uso eficiente de los recursos transitando hacia una economía circular, resiliente frente al cambio climático y basada en la reducción de residuos nocivos. Eso implica la implementación de medidas que promuevan la prevención de la contaminación ambiental, reduciendo la huella de CO_2 o las emisiones de compuestos peligrosos.

Entre los compuestos nocivos emitidos a la atmósfera a partir de fuentes antropogénicas se encuentran los derivados de silicio como los siloxanos. Los siloxanos son compuestos esenciales que se emplean en un amplio número de sectores industriales y en la fabricación de una gran cantidad de productos de mercado. El extenso uso de estos compuestos deriva en la emisión de metilsiloxanos volátiles (MSV) a la atmósfera, así como en la descarga de siloxanos a vertederos y estaciones depuradoras de aguas residuales donde los MSV se transfieren finalmente al aire o al biogás producido en la digestión anaerobia. El efecto potencialmente tóxico de estas emisiones se ha demostrado en la bioacumulación de MSV, afectando al tracto respiratorio y al sistema reproductivo de algunos animales. Además, se han clasificado recientemente como compuestos que dan lugar a biomagnificación en la red trófica acuática y terrestre. Más allá de sus efectos nocivos, la presencia de MSV en el biogás se traduce en un alto impacto económico durante su valorización como energía renovable debido a la oxidación de los MSV a dióxido de silicio (SiO_2) durante su combustión, un depósito cristalino que provoca la corrosión en motores y turbinas.

Por todo ello, existe un creciente interés en desarrollar tecnologías eficientes, sostenibles y rentables para el tratamiento y mitigación de las emisiones de MSV. Los procesos físico-químicos son hoy en día las tecnologías más eficientes para la eliminación de dichos residuos, sin embargo, estas tecnologías se caracterizan por sus altos costes de operación y mantenimiento, y por su elevada huella de carbono. Por el contrario, las biotecnologías, basadas en la degradación de los MSV por acción catalítica biológica, representan una alternativa de bajo coste y respetuosa con el medio ambiente para el tratamiento de los MSV de corrientes gaseosas. Sin embargo, la baja solubilidad de los MSV en la fase acuosa de los biorreactores, donde los microorganismos responsables de su degradación captan el contaminante, reduce la eficiencia de estas tecnologías y por lo tanto limita su implementación.

Esta tesis se centra en el diseño y optimización de los parámetros de operación de biorreactores novedosos de alta transferencia, como el biofiltro percolador bifásico, con el fin de mejorar el tratamiento de MSV reduciendo la limitación de transferencia de materia asociada a los MSV. Además, las comunidades microbiológicas involucradas en el proceso de degradación también serán estudiadas en esta tesis.

En el **Capítulo 3** se evaluó comparativamente la eliminación de los MSV más comunes (hexametildisiloxano, L2; octametiltrisiloxano, L3; octametilciclotetrasiloxano, D4; y decametilciclopentasiloxano, D5) en condiciones aerobias en un biofiltro percolador convencional (BFP) y en un BFP bifásico (2F-BFP) utilizando aceite de silicona al 30% vol. como fase orgánica. El 2F-BFP mostró un rendimiento superior en comparación con el BFP convencional, aumentando la eficacia de eliminación (EE) total de los MSV de 30 % en el BFP hasta ~70 % en el 2F-BFP. Las EEs más altas en el 2F-BFP se registraron para el D4 y el D5, alcanzando valores de 80-90% y capacidades de eliminación (CEs) de 0,12 - 0,17 g $m^{-3} \cdot h^{-1}$. Se obtuvieron valores ligeramente inferiores para L3 (70-80%), y el rendimiento más bajo se registró para L2 (20-60%) debido a la alta presión de vapor de este siloxano y por tanto a su menor afinidad por la fase orgánica. A pesar de los diferentes inóculos utilizados, se encontró una comunidad microbiana similar al final de la operación de ambos BFPs, con el clado *Acidithiobacillacea KCM-B-112* y los géneros *Reynarella* y *Chitinophaga* como bacterias dominantes, lo que sugiere una especialización de los microorganismos relacionados con la degradación de siloxanos.

Una vez comprobada la mayor eficacia de los sistemas bifásicos para la eliminación de estos MSV, es necesario determinar las condiciones de operación que permitan obtener un mayor rendimiento del sistema. Con este objetivo, en el **Capítulo 4** se estudió el rendimiento de eliminación de siloxanos (D4, D5, L2 y L3) de un 2F-BFP en condiciones aerobias en función del tiempo de residencia en lecho vacío (TRLV) y de la fracción de la fase orgánica (aceite de silicona) utilizadas. Se observó una disminución en la eliminación total de los MSV de 76 a 49% cuando el TRLV se redujo de 60 a 15 min. Las eliminaciones más altas se lograron para el D4 (53-84%) y el D5 (69-87%), en comparación con los valores más bajos registrados para el L2 (19-45%) y el L3 (31-81%). El aumento de la proporción de aceite de silicona en el medio mineral recirculado del 5 al 45% dio como resultado una mejora de la eliminación total de MSV del 35 al 52%, trabajando a un TRLV de 60 min. Esta mejora se observó para el L3 (21-50%), el D4 (26-64%) y el D5 (58-78%), mientras que las eliminaciones del L2 permanecieron < 25%. Al final del experimento se obtuvo una comunidad bacteriana altamente especializada dominada de nuevo por organismos no cultivables pertenecientes al clado *Acidithiobacillacea KCM-B-112.*

La eliminación biológica de siloxanos en corrientes sin disponibilidad de oxígeno como aceptor de electrones constituye otra área de gran interés, principalmente orientada a la reducción de estos contaminantes cuando están presentes en el biogás. Por ello, en el

Capítulo 5 se investigó por primera vez la viabilidad de la biodegradación anóxica de siloxanos (L2, L3, D4 y D5) en un 2F-BFP utilizando aceite de silicona como fase orgánica. Se evaluó la influencia de la proporción de aceite de silicona y la concentración de entrada de siloxanos. Las eliminaciones más altas se obtuvieron para el D4 (41-54%) y el D5 (48-73%). Se registraron menores eliminaciones para el L2 (12-15%) y el L3 (22-38%) como consecuencia de su mayor volatilidad. El mejor rendimiento se obtuvo para un contenido de aceite de silicona del 45%. Duplicando la carga de entrada se mejoró la CE del 2F-BFP en un 50 %, aunque las EEs no variaron. La degradación anóxica de los siloxanos se atribuyó al consorcio de bacterias especializadas dominado por el clado *Acidithiobacillacea KCM-B-112* y los géneros *Parvibaculum, Zarvazinia, Arenimonas, Moraxellaceae* y *Luteimonas*.

Finalmente, tras comprobar la mayor eficiencia de los sistemas bifásicos y confirmar que el transporte de los contaminantes constituye la etapa limitante del proceso, se llevó a cabo un estudio final con el objetivo de aumentar las eficacias de eliminación obtenidas. Para ello, en el **Capítulo 6**, se optimizaron dos parámetros de operación en dos 2F-BFPs aerobio y anóxico (la velocidad del líquido recirculado (TLV) y la recirculación interna del gas) para obtener un mejor transporte de siloxanos. Los resultados obtenidos mostraron que el aumento de la TLV de 2 a 10 m h^{-1} resultó en una mayor EE tanto en condiciones anóxicas como aerobias, alcanzando valores máximos de 55 y 47%, respectivamente. Este efecto fue más significativo para los siloxanos lineales. Por el contrario, un aumento adicional en la TLV a 20 m h^{-1} junto con la implementación de la recirculación interna del gas provocó una turbulencia excesiva en la solución de riego, desprendiendo la biopelícula y suponiendo un efecto negativo para la EE. Los siloxanos cíclicos fueron eliminados de manera más efectiva (se registraron EEs máximas del 75% para el D5), si bien las modificaciones del sistema ejercieron un efecto menor sobre su eliminación. La población bacteriana activa involucrada en la degradación de los siloxanos (estudiada mediante extracción y secuenciación del ARN) estuvo dominada por el clado *Acidithiobacillacea KCM-B-112* y el género *Parvibaculum* en condiciones aerobias, mientras que los miembros de la familia *Phyllobacteriacea* y los géneros *Nocardia* y *Baekduia* dominaron en condiciones anóxicas.

La implementación a gran escala de las tecnologías biológicas de eliminación de siloxanos es necesaria para demostrar su competitividad respecto a las actuales tecnologías comerciales físico-químicas desde el punto de vista técnico, económico y medioambiental. Para ello, en el **Capítulo 7** se evaluó la viabilidad tecno-económica y ambiental de la biofiltración en un BFP frente a las tecnologías más comúnmente empleadas para la eliminación de siloxanos: adsorción en carbón activado y absorción química, incluyendo una configuración híbrida que consiste en un BFP seguido de una etapa final basada en adsorción en carbón activo. Si bien el estado aún incipiente de las tecnologías biológicas para la eliminación de siloxanos dificulta esta evaluación, los resultados de este estudio demostraron que las biotecnologías superan a las tecnologías físico-químicas de eliminación de siloxanos desde un punto de vista tanto económico como ambiental, alcanzando los menores costes de operación (1.2 €/ $(m^3/h)^{-1}$) y una huella de carbono (2.0×10^{-4} kg CO_2 eq. m^{-3}).

Finalmente, en el **Capítulo 8**, se incluye el diseño y los resultados de la operación de un 2F-BFP a escala piloto de 104 L de volumen para la eliminación de MSV de una corriente de biometano con un rango de flujo de 2.7-8 m^3 d^{-1} situado en exterior en el Centro de Innovación Tecnológica de Residuos “Alfonso Maíllo” (CIAM, URBASER). A pesar de las condiciones adversas de operación, la concentración de MSV en el biometano tratado se mantuvo entre 9 y 11 mg m^{-3}, cumpliendo finalmente con la concentración de MSV objetivo impuesta por la legislación europea (EN 16723). D4 y D5 fueron los siloxanos

más abundantes en el biometano no tratado, representando entre un 4 - 30% y un 30 - 94% del total de siloxanos, respectivamente. Las eliminaciones máximas de D4 y D5 (67% y 52%, respectivamente) en el 2F-BFP a escala piloto se registraron durante el último periodo de operación, cuando la fracción de aceite de silicona en la solución líquida recirculada aumentó de 10 a 20%.

Los resultados obtenidos en esta tesis demostraron la viabilidad de las tecnologías biológicas de alta transferencia, en concreto de los sistemas bifásicos, como alternativas innovadoras para la eliminación de MSV. Los 2P-BFP se establecen así como una nueva vía para el tratamiento de emisiones atmosféricas y corrientes de biogás contaminadas con siloxanos, debido a su reducido impacto ambiental y su bajo coste frente a otros procesos físico-químicos.

Abstract

Nowadays, environmental problems such as climate change, the formation of tropospheric ozone, the overuse of natural resources or atmospheric pollution constitute one of the greatest concerns worldwide. The policies and strategies currently enforced, such as the European Green Deal, are focused on boosting the efficient use of resources by moving towards a clean and circular economy, resilient to climate change and based on the reduction of harmful waste. This implies the implementation of measures that promote the prevention of environmental pollution by reducing the CO_2 footprint and the emissions of hazardous compounds.

Silicon derivatives such as siloxanes are among the harmful compounds emitted into the atmosphere from anthropogenic sources. Siloxanes are essential building block materials employed in several industrial sectors and in the manufacture of a large number of consumer products available in the market. This fact results in the emissions of volatile methyl siloxanes (VMS) to the atmosphere, along with their release into landfills and wastewater treatment plants ending up either in the air or in the biogas produced in anaerobic digestion. The potential toxic effect of these emissions has been proved in the bioaccumulation of VMS, affecting the respiratory tract and reproductive system of some animals. Moreover, they have been recently classified as potential compounds responsible for trophic magnification in aquatic and terrestrial food chains. Beyond their harmful effects, their presence in biogas entails a high economic impact during its valorisation as renewable energy due to the oxidation of VMS to silicon dioxide (SiO_2) during biogas combustion, a crystalline deposit that causes corrosion of engines and turbines.

In this context, there is a growing interest to develop efficient, sustainable and cost-effective technologies for the treatment and abatement of VMS emissions. Physical-

chemical processes appear nowadays as the most efficient technologies for the removal of VMS from gaseous emissions. However, these technologies are characterized by their high operating and maintenance costs, along with their high carbon footprint. On the contrary, biotechnologies based on the biodegradation of VMS by the biological catalytic activity, represent a low cost and environmentally friendly alternative for the treatment of VMS gaseous emissions. However, the low solubility of these compounds in the aqueous phase of bioreactors, where the microorganisms responsible for their degradation uptake the pollutant, reduces the removal efficiency (RE) of these technologies and therefore limits their implementation.

The present thesis focusses on the design and optimization of the operating parameters of novel high mass transfer bioreactors, such as two-phase partitioning biotrickling filter, with the aim of improving the removal of VMS by reducing the limitation of mass transfer associated with VMS. In addition, the microbial community involved in the degradation process were also investigated.

For this purpose, **Chapter 3** comparatively evaluated the removal of the most common VMS (hexamethyldisiloxane, L2; octamethyltrisiloxane, L3; octamethylcyclotetrasiloxane, D4; and decamethylcyclopentasiloxane, D5) under aerobic conditions in a conventional biotrickling filter (BTF) and a two-phase partitioning BTF (TP-BTF) with silicone oil at 30% (v/v) as organic phase. The TP-BTF showed a superior performance compared to the conventional BTF, supporting a 40% higher total VMS RE. The highest REs in the TP-BTF were recorded for D4 and D5, reaching values of 80-90%, corresponding to ECs between 0.12 and 0.17 g $m^{-3}\cdot h^{-1}$. Slightly lower values were obtained for L3 (70-80%), and the lowest performance was recorded for L2 (20-60%). This was attributed to the high vapour pressure of this siloxane, and therefore its lower affinity for the organic phase. Surprisingly, despite the different inoculum used, a similar microbial community was found by the end of the operation of both BTFs, with the clade *Acidithiobacillacea KCM-B-112* and the genera *Reynarella* and *Chitinophaga* as the dominant bacteria.

Once the superior performance of biphasic systems for the elimination of siloxanes was confirmed, it was necessary to determine the operating conditions supporting a better VMS abatement performance. To this aim, **Chapter 4** studied the influence of the empty bed residence time (EBRT) and the fraction of the organic phase (silicone oil) on the removal performance of four model siloxanes (D4, D5, L2 and L3) in a TP-BTF under aerobic conditions. A decrease in the total VMS removal from 76 to 49% was observed when the EBRT was reduced from 60 to 15 min. The highest removals were achieved for D4 (53-84%) and D5 (69-87%), compared to the lower values recorded for L2 (19-45%) and L3 (31-81%). The increase in the percentage of silicone oil in the recycling mineral medium from 5 to 45 % resulted in an improvement of the total VMS abatement from 35 to 52 % working at an EBRT of 60 min. This enhancement was observed for L3 (21-50%), D4 (26-64%) and D5 (58-78%), whereas L2 removals remained < 25%. A highly specialized bacterial community dominated by the clade *Acidithiobacillacea KCM-B-112* was retrieved at the end of the experiment.

The biological removal of siloxanes in gaseous streams in the absence of oxygen as electron acceptor is another area of great interest, mainly aimed at reducing the concentration of these pollutants when present in biogas. Thus, **Chapter 5** investigated for the first time the feasibility of the anoxic biodegradation of siloxanes (L2, L3, D4 and D5) in a TP-BTF using silicone oil as the organic phase. The influence of the silicone oil fraction and the inlet concentration of siloxanes were also evaluated. The highest removals were obtained for D4 (41-54%) and D5 (48-73%). Lower removals were recorded for L2 (12-15%) and L3 (22-38%) as a result of their higher volatility. The best performance was obtained at a silicone oil fraction of 45%. Doubling the inlet load enhanced the elimination capacity of the TP-BTF by 50%, although the removal efficiencies did not vary. A specialized bacteria consortium dominated by the clade *Acidithiobacillacea KCM-B-112* and the genera *Parvibaculum*, *Zarvazinia*, *Arenimonas*, *Moraxellaceae* and *Luteimonas* was related to anoxic siloxanes degradation.

Finally, after confirming the greater efficiency of the two-phase partitioning systems and the mass transport of VMS as the limiting step of the process, a final study was carried out with the aim of increasing the removal efficiencies obtained. To this aim, two parameters were optimized in **Chapter 6** in aerobic and anoxic TP-BTFs (the trickling liquid velocity (TLV) and the internal gas recirculation) in order to boost the mass transport of siloxanes to the liquid phase. The results obtained showed that the increase in TLV from 2 to 10 m h^{-1} resulted in higher REs under both anoxic and aerobic conditions, reaching maximum values of 55 and 47%, respectively. This effect was more significant for the linear siloxanes. On the contrary, a further increase in the TLV to 20 m h^{-1} together with the implementation of internal gas recirculation caused an excessive turbulence in the liquid side, detaching the biofilm and entailing a negative effect on the RE. The cyclic siloxanes were more effectively eliminated (maximum REs of 75% were recorded for decamethylcyclopentasiloxane (D5)), but the studied system modifications exerted a minor effect on their RE. The active bacterial population involved in siloxanes degradation (studied through RNA extraction and sequencing) was dominated by the clade *Acidithiobacillacea KCM-B-112* and the genus *Parvibaculum* under aerobic conditions, while the members of the family *Phyllobacteriacea* and the genera *Nocardia* and *Baekduia* dominated under anoxic conditions.

The large-scale implementation of biological siloxane removal technologies is required to demonstrate their competitiveness and sustainability compared to current commercial physical-chemical technologies from a technical, economic and environmental point of view. In this sense, **Chapter 7** assessed the techno-economic and environmental feasibility of biofiltration in a BTF versus conventional physical-chemical processes for the removal of siloxanes: activated carbon adsorption and chemical absorption. A hybrid configuration consisting of a BTF coupled with a polishing step based on activated carbon adsorption was also evaluated. The results of this study showed that biotechnologies outperform physical-chemical siloxane removal technologies from both an economic and an environmental point of view, reaching the lowest operating costs (1.2 €/ $(m^3/h)^{-1}$) and carbon footprint (2.0×10^{-4} kg CO_2 eq. m^{-3}).

Finally**,** the results of the operation of a pilot-scale TP-BTF of 104 L devoted to the removal of VMS from a biomethane stream of 2.7-8 m^3 d^{-1} constructed in the Waste Technological Innovation Center "Alfonso Maíllo" (CIAM, URBASER) are included in **Chapter 8**. Despite the adverse operational conditions, the VMS concentration in the treated biomethane remained between 9 and 11 mg m^{-3}, finally complying with the target VMS concentration imposed by the European biomethane standard. D4 and D5 were the most abundant siloxanes in the untreated biogas, representing from 4 to 30% and from 30 to 94% of the total siloxanes, respectively. The maximum removals of both D4 and D5 (67% and 52%, respectively) were recorded during the last operation period, when the silicone oil fraction in the trickling liquid solution was increased from 10 to 20%.

The results obtained in this thesis demonstrated the feasibility of high mass transfer biological technologies, especially two-phase partitioning systems, as an innovative alternative for the removal of VMS. TP-BTFs thus stand as a new platform to abate siloxanes from aerobic atmospheric emissions and biogas due to their reduced environmental impact and their low cost compared to physical-chemical processes.

List of publications

The following publications are presented within the scope of this thesis. Publications 1-3 have been published in international journals indexed in Clarivate Analytics' Web of Science (WoS). Publication 4 has been submitted for publication.

1. Pascual, C., Cantera, S., Muñoz, R., Lebrero, R., 2020. Comparative assessment of two biotrickling filters for siloxanes removal: Effect of the addition of an organic phase. Chemosphere 251, 126359. https://doi.org/10.1016/j.chemosphere.2020.126359

2. Pascual, C., Cantera, S., Muñoz, R., Lebrero, R., 2021. Siloxanes removal in a two-phase partitioning biotrickling filter: influence of the EBRT and the organic phase. Renew. Energy 177. https://doi.org/10.1016/j.renene.2021.05.144

3. Pascual, C., Cantera, S., Muñoz, R., Lebrero, R., 2022. Innovative polishing stage in biogas upgrading: Siloxanes abatement in an anoxic two-phase partitioning biotrickling filter. J. Clean. Prod. 371. https://doi.org/10.1016/j.jclepro.2022.133427

4. Pascual, C., Cantera, S., Muñoz, R., Lebrero, R., 2022. Assessment of the mass transfer strategy and the role of the active bacterial population on the biological degradation of siloxanes (submitted).

Contribution to the articles included in the thesis

In all the publications included in this thesis (**Papers 1, 2, 3 and 4**), I was responsible for the design and operation of the experimental set-up under the supervision of Dr. Raquel Lebrero and Dr. Raúl Muñoz. I also performed the formal analysis of the results from bioreactors. Dr. Sara Cantera supported the analysis of the microbial population and community dynamics. I wrote the first draft of all the original manuscripts. The review and edition of the original manuscripts were conducted by Dr. Raquel Lebrero, Dr. Sara Cantera and Dr. Raúl Muñoz.

Chapter 1.

Introduction

Part of the content of this chapter was adapted from:

Ángeles Torres, R., Marín, D., Rodero, M. del R., **Pascual, C**., González-Sanchez, A., de Godos Crespo, I., Lebrero, R., Torre, R.M., 2020. Biogas treatment for H_2S, CO_2, and other contaminants removal. From Biofiltration to Promising Options Gaseous Fluxes Biotreatment 153–176. https://doi.org/10.1016/B978-0-12-819064-7.00008-X

Pascual, C., Cantera, S., Lebrero, R., 2021. Volatile Siloxanes Emissions: Impact and Perspectives. Trends Biotechnol. 39, 1245–1248. https://doi.org/10.1016/j.tibtech.2021.05.003

Pascual, C., Lebrero, R., Cantera, S., 2022b. Toward a sustainable and cost-efficient biological-based platform for siloxanes removal. Crit. Rev. Environ. Sci. Technol. 1–17. https://doi.org/10.1080/10643389.2022.2044254

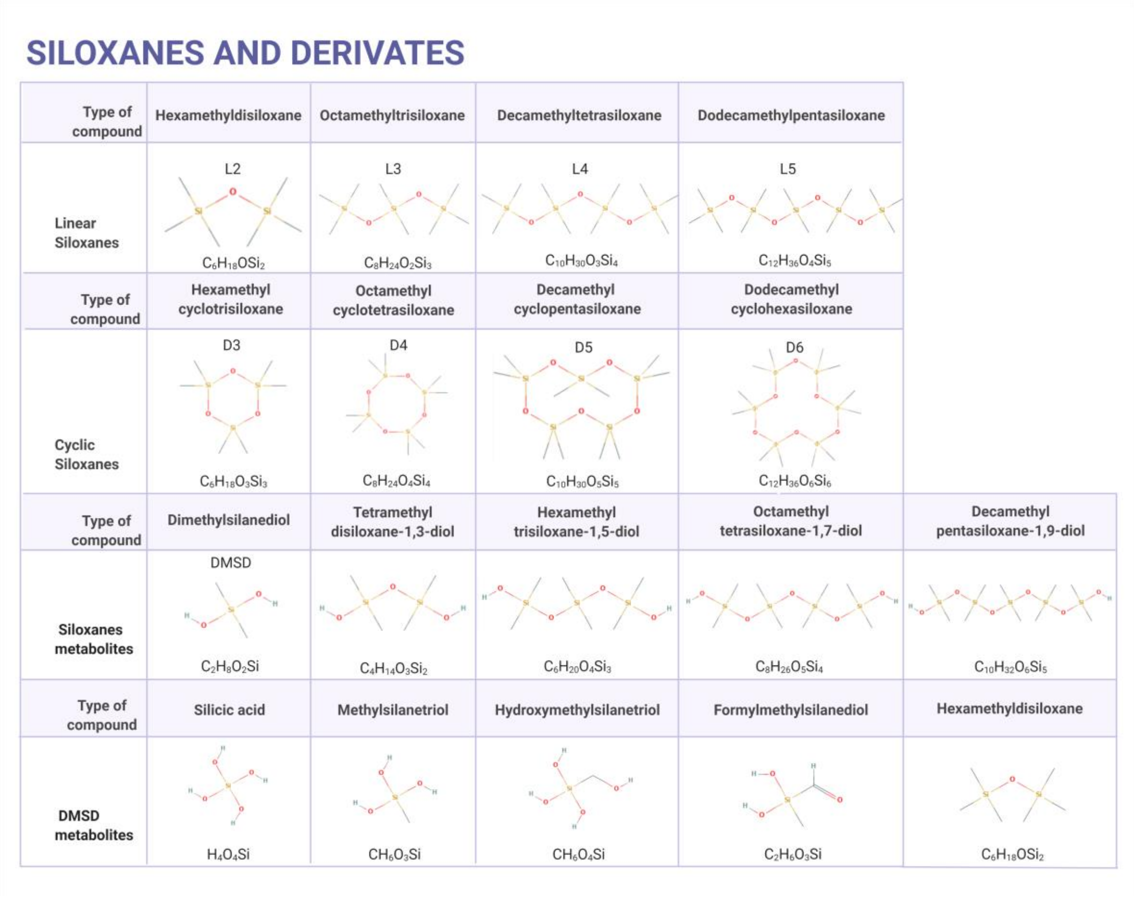
1.1 Volatile methyl siloxanes: damaging compounds during biogas energetic valorization.

1.1.1 Siloxanes chemical structure and classification

One of the most persistent anthropogenic trace components emitted to the environment are volatile methyl siloxanes (VMS). VMS consist of volatile, low and medium molecular weight compounds (<500 g mol^{-1}) that contain in their structure silicon, carbon and oxygen atoms in the form of $-Si(CH_3)_2-O-$ units with a silicon atom bonded to at least one carbon and one oxygen atom (Rücker and Kümmerer, 2015). They are classified into linear and cyclic VMS (L or D, respectively) according to their structure (Table 1), followed by a number that indicates the amount of silicon atoms contained in the molecule (Foppiano et al., 2019). Another silicon compound usually classified within the group of siloxanes is trimethylsilanol (TMSOH), a compound with greater solubility in water as a result of the presence of a –OH group bonded directly to the Si atom (Piechota, 2021).

The large covalent radius of the Si atom is responsible for the larger Si bonds length (with C and other elements) compared to the bond of the other elements. Moreover, this bond is characterised by its moderate polarity. The methyl groups that constitute the structure of siloxanes, together with the weak intermolecular forces between methylsiloxane chains and the high flexibility of the Si−O−Si bond, are responsible for their useful properties such as low solubility, high compressibility, low flammability, low surface tension, water repelling properties and high thermal stability (Dewil et al., 2006; Piechota, 2021; Rücker and Kümmerer, 2015).

Table 1. Most common siloxanes and their potential biodegradation products.



SILOXANES AND DERIVATES

Type of compound	Hexamethyldisiloxane	Octamethyltrisiloxane	Decamethyltetrasiloxane	Dodecamethylpentasiloxane	
Linear Siloxanes	L2 $C_6H_{18}OSi_2$	L3 $C_8H_{24}O_2Si_3$	L4 $C_{10}H_{30}O_3Si_4$	L5 $C_{12}H_{36}O_4Si_5$	
Type of compound	Hexamethyl cyclotrisiloxane	Octamethyl cyclotetrasiloxane	Decamethyl cyclopentasiloxane	Dodecamethyl cyclohexasiloxane	
Cyclic Siloxanes	D3 $C_6H_{18}O_3Si_3$	D4 $C_8H_{24}O_4Si_4$	D5 $C_{10}H_{30}O_5Si_5$	D6 $C_{12}H_{36}O_6Si_6$	
Type of compound	Dimethylsilanediol	Tetramethyl disiloxane-1,3-diol	Hexamethyl trisiloxane-1,5-diol	Octamethyl tetrasiloxane-1,7-diol	Decamethyl pentasiloxane-1,9-diol
Siloxanes metabolites	DMSD $C_2H_8O_2Si$	$C_4H_{14}O_3Si_2$	$C_6H_{20}O_4Si_3$	$C_8H_{26}O_5Si_4$	$C_{10}H_{32}O_6Si_5$
Type of compound	Silicic acid	Methylsilanetriol	Hydroxymethylsilanetriol	Formylmethylsilanediol	Hexamethyldisiloxane
DMSD metabolites	H_4O_4Si	CH_6O_3Si	CH_6O_4Si	$C_2H_6O_3Si$	$C_6H_{18}OSi_2$

1.1.2 Production, discharge and impact of siloxanes

The valuable properties of siloxanes make them an essential building block for multiple sectors of great interest. In this sense, siloxanes are extensively used in industrial applications (i.e. construction, electronics, automotive industry, textile, medical equipment, food packaging, pharmaceutical or cosmetics industry) and in household products (i.e. detergents, shampoos, cosmetics, paper coatings and textile goods) (Dewil et al., 2006). Thus, the manufacture of siloxanes based products has reached an annual production of millions of tons with an expected annual increase of ~6.5% in the next few years.

Most of these silicones are released to the environment as high molecular weight compounds, polydimethylsiloxanes (PDMS), that are subsequently hydrolyzed to VMS. More than 90% of all the VMS entering the environment end up in the atmosphere (Tansel and Surita, 2017). These emissions exhibit a large variability in the type and abundance of VMS. In general, cyclic siloxanes (D4-D6) are the most abundant, D4 representing 60% of the total VMS (Ruiling et al., 2017).

Sources of siloxanes in the atmosphere are either direct discharges, among which the emissions from the silicone manufacturing industry or siloxanes accumulated in residential indoor air and other microenvironments are included; or indirect discharges, i.e. volatile siloxanes transferred from water bodies to the atmosphere, and volatile siloxanes from sewage and solid waste that are emitted along with biogas and waste off-gases to the atmosphere (Horii and Kannan, 2020). In the particular case of residual siloxanes contained in sewage and solid waste, a high proportion of VMS (~68%) remains adsorbed onto the sludge and extracellular polymeric substances due to the low solubility of VMS (Bletsou et al., 2013; Shen et al., 2018), being subsequently volatilized during the anaerobic digestion of the sludge. As a consequence, these VMS end up in the produced biogas (Guo et al., 2021) (Figure 1).

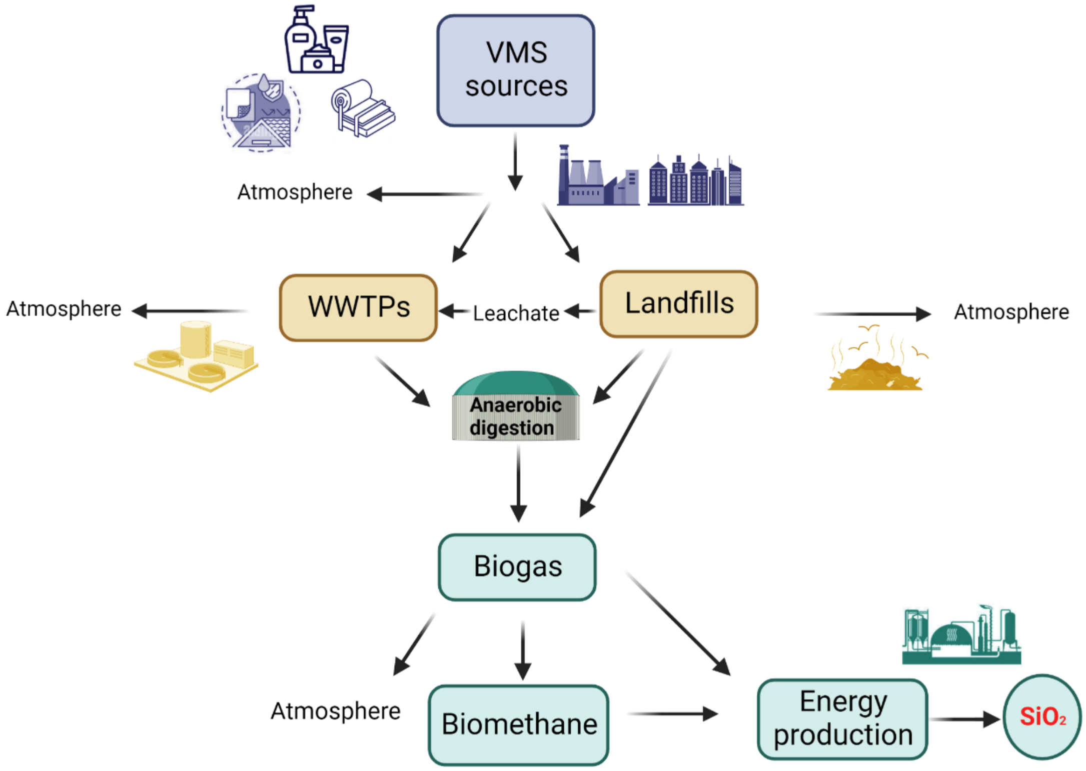


Figure 1. Environmental fate of siloxanes (black arrows) in WWTPs and landfills, and their occurrence in biogas (adapted from Shen el al. (2018)).

Direct discharges of VMS to the atmosphere might have a detrimental impact on the environment and human health. Recent research claims that VMS should be classified as emerging environmental pollutants (Horii and Kannan, 2020; Mojsiewicz-Pieńkowska and Krenczkowska, 2018). Despite the human health effects derived from VMS exposure are not well understood, several studies have revealed that VMS are potentially toxic to living organisms. In this context, they affect animals' reproductive systems, are carcinogenic, and harm the respiratory tract at high doses (T. M. Tran et al., 2019). Moreover, these compounds have been recently classified as potential compounds responsible for trophic magnification in aquatic and terrestrial food web (Cui et al., 2019; Fremlin et al., 2021).

In addition, VMS have important economic implications in certain processes. While the concentration of VMS in gas emissions from waste treatment plants is in the range of 0.1-20 µg m^{-3}, it might increase up to 400 mg m^{-3} in the case of biogas (Ángeles Torres et al., 2020; Gaj and Pakuluk, 2015; Wang et al., 2019). If subsequent gas treatment involves combustion (for example during the energetic valorization of the produced biogas), VMS are oxidized to CO_2 and silicone dioxide (SiO_2), resulting in deposits of abrasive micro particulates of crystalline SiO_2 (Equation 1). These silica particles lead to erosion and corrosion of several equipment devices (boilers, fuel cells, internal combustion engines or turbines) and clogging of pipes.

$$((CH_3)_2SiO)_n + 4nO_2 \rightarrow n\ SiO_2 + 2nCO_2 + 3nH_2O \qquad \textbf{Equation 1}$$

Where *n* indicates the numbers of Si atoms (n = 3–6) (Ruiling et al., 2017).

Besides increasing the maintenance costs, the modification of the combustion chamber geometry triggers higher emissions of carbon monoxide and formaldehyde, likely failing to comply with air emissions regulations (Ajhar et al., 2010). Thus, the accumulation of silica has a strong negative economic impact in waste facilities, which devalues biogas and restrains its use in production plants (for example, it has been estimated that the removal of siloxanes in a wastewater treatment plant facility can save between 2.6 and 5.7 €/$(m^3\ d^{-1})_{\text{treated wastewater}}$ in operating costs per year) (McCarrick, 2012).

Nevertheless, due to their unique physicochemical properties and functionalities, siloxanes are irreplaceable in many areas. Although legal restrictions on siloxane emissions into the atmosphere have not been established, the maximum concentration required for the injection of biomethane into the natural gas grid and for its use as a vehicle fuel according to European legislation is ∼10 mg m^{-3} (Standardization, 2016). Hence, VMS abatement is of utmost importance not only to reduce the atmospheric emissions of these emerging pollutants, but also for biogas energetic valorization.

1.2 Commercial technologies for siloxanes abatement

VMS removal technologies employed to date are based on physical-chemical processes: adsorption, absorption, cryogenic condensation, catalytic processes and membrane separation (Table 2).

Adsorption is an easy-to-operate technology widely used in industrial applications. Among the adsorbent materials studied, activated carbon and silica gel are the most commonly employed. Activated carbon is a low cost material with a high adsorption capacity and VMS removal efficiencies (REs) of ~ 99 %. Nevertheless, activated carbon is not a selective adsorbent material and other compounds present in biogas, such a H_2S and water, compete with VMS for adsorption, thus resulting in a rapid saturation of the adsorbent. Silica gel is also an excellent adsorbent, with an adsorption capacity up to 10 times higher than that of activated carbon and an easier regeneration (RE up to 98%) (Soreanu et al., 2011). Other adsorbent materials are based on molecular sieves, activated aluminium oxides or alkaline oxides. In general, adsorption is a highly effective technology for VMS removal (RE > 90 % regardless of the adsorbent material (Shen et al., 2018)) , although at the expenses of high operating cost and high carbon footprint associated to the regeneration or replacement of the adsorbent.

Regarding absorption processes, both physical and chemical absorption in organic and inorganic solvents, respectively, have been studied. Organic solvents, such as selexol and tetradecane, have been successfully studied as physical absorbents, reaching REs between 97 and 99 % (Rene Huppmann et al., 1996; Wheless and Pierce, 2004). Despite their satisfactory performance, the use of organic solvents is costly and requires cooling to avoid solvent losses and prevent atmospheric emissions (Gaj, 2017). Conversely, chemical absorption allows for VMS elimination via breaking Si-O bonds using concentrated alkaline or acid solutions. Acid solutions are preferred over alkaline due to the alkaline deposits formed as a result of the interaction between –OH radicals from the solution and CO_2. REs higher than 95 % have been reported when working at 60 ºC with acid solutions. In spite of the good performance, this technology is difficult to implement due to the corrosive nature of acid solutions, which increases both the investment costs and the environmental impact (Shen et al., 2018).

Cryogenic condensation or deep chilling is based on the condensation of VMS by cooling processes. The VMS removal performance achieved significantly depends on the operating temperature: whereas removals of 12-25 % have been obtained when operating at 5 ºC, these values increased up to 25.9 and 99.3 % when reducing the operating temperature to -25 and -70 ºC, respectively (Shen et al., 2018). These extreme operating conditions make this technology economically unfeasible unless high flow rates and high VMS concentrations are treated (Ajhar et al., 2010).

Membrane separation can be also used as a VMS removal technology. In this sense, polydimethylsiloxane has been identified as a suitable membrane material for VMS separation from raw biogas (Basu et al., 2010). This dense polymeric membrane material retains biomethane while allowing the permeation of VMS and other undesirable compounds such as water or volatile organic compounds (VOC). VMS removals of ~80 % have been recorded for this kind of membranes. The main disadvantage of this technology is the high investment associated to the membrane material and the energy cost related to the compressors or vacuum pumps (Shen et al., 2018).

Finally, catalytic processes are based on the adsorption and subsequent thermal decomposition of VMS over solid oxides. Both basic and acid oxides such as CaO, MgO, Al_2O_3, and SiO_2 have been studied as catalysts, working between 200 and 400 ºC. However, no satisfactory removals have been achieved to date (Finocchio et al., 2008). The main issue of catalytic processes is the irreversible and rapid deactivation of the catalysts due to microcrystalline silica deposition on the catalyst surface. In this context, a combined use of two catalysts, Al_2O_3 and V_2O_5/TiO_2, has been suggested by Urban et al. (Urban et al., 2009). V_2O_5/TiO_2 is employed to first remove a wide range of detrimental minor organic compounds, although it could be deactivated by VMS. Thus, the addition of Al_2O_3 as a preliminary catalyst upstream of the process will protect the subsequent catalyst and avoid its deactivation. Almost complete VMS removal from biogas has been initially recorded using this two-stage catalytic system. Nevertheless, this removal gradually decreased to 9 % after 35 hours of operation due to the deactivation of Al_2O_3 (Urban et al., 2009).

With the aim of overcoming the high operating costs and environmental impacts of physical-chemical technologies for VMS abatement, recent advances on these techniques have focused on the development and optimization of commercial adsorbents, as the main challenge relies on increasing the breakthrough adsorption capacity of the sorption material. For example, enhancing the activation process or the pore size of activated carbon increases the adsorption capacity, while reducing the replacement cost. In the case of silica gel, it has been observed that micro/mesoporous silica gels can increase the adsorption capacity of conventional technologies (Meng et al., 2020b). Other critical parameters are the physical-chemical properties of the adsorbent and its regeneration. Textural properties such as the presence of functional groups or inorganic impurities like alkali metals (K, Na) determine the amount of hydrophilic sites, that ultimately reduce both VMS adsorption capacity in the presence of humidity and the regeneration capacity distinctive of siloxanes polymerization on the adsorbent (Tran et al., 2018; Tran et al., 2019a, 2019b). Moreover, the use of activated carbon with functionalized mixed transition metal oxides (such as the commercial SulfaTrap R8$^{®}$) seems to have superior VMS removal capacities (Calbry-Muzyka et al., 2019). In the case of silica gels, the meso-/microporous structure and hydrophobic surface of acetylated and methyl-functionalized silica gels showed adsorption levels and breakthrough times up to 18 times higher compared to conventional silica gel (Liu et al., 2019; Meng et al., 2020a).

Overall, these tailored materials have demonstrated enhanced siloxanes adsorption capacities compared to conventional adsorbent materials (Bak et al., 2019a, 2019b). However, further steps on adsorption alternatives must target also at increasing the sustainability of the process. For instance, the valorization of solid waste as raw material (wood waste, lignocellulosic waste) for sorbents production has been recently assessed. These studies suggested that the adsorbents obtained could achieve performances comparable or even higher than those of commercial activated carbons in an environmentally friendly way (Papurello et al., 2019, 2018).

Although these novel advances in physical-chemical technologies have improved the economic and environmental sustainability of the VMS removal process, they still exhibit high investment and operating costs (see Table 2), and detrimental environmental impacts which runs against the principles of sustainability. Thus, biodegradation technologies, although in an embryonic stage when applied to siloxanes abatement, could certainly play a key role to overcome the main limitations of physical-chemical processes.

Table 2. VMS removal performance and main techno-economic and environmental aspects of siloxanes treatment technologies. Investment cost (k€ Nm^{-3} h^{-1}): < 0.5 (low), 0.5–1 (medium), >1 (high). Operating cost (c€ Nm^{-3}): < 1.5(low), 1.5–3 (medium), > 3 (high).

Technology		**Siloxanes RE (%)**	**Investment cost**	**Operating cost**	**Advantages**	**Disadvantages**	**References**
Adsorption	Activated carbon, silica gel, molecular sieves, zeolites, metal oxides	90-99	Low	Medium	• Highly effective technology. • Easy to operate. • Possibility of simultaneous removal of trace compounds.	• High operating cost associated to the regeneration or replacement of the adsorbent.	Shen et al. (2019) Gaj. (2017) Arespacochaga et al. (2015)
Absorption	Physical absorption: Organic solvent (Selexol^{TM} and tetradecane) Chemical absorption: Inorganic solvent (concentrated alkaline or acid solutions)	97- 99 (organic solvent) < 95 (inorganic solvent)	Medium	High	• Highly effective technology. • Chemical absorption also degrades siloxanes.	• Organic solvents are costly. Requires cooling to avoid solvent losses and prevent atmospheric emissions. • Deposits formed as a result of the interaction between –OH radicals from the solution and CO_2 from biogas. • Corrosive nature of acidic solutions, which increases both the investment costs and the environmental impact. • Risk of desorption at high fluctuations in temperature and VMS concentration.	Shen et al. (2019), Huppmann et al.(1996) Wheless and Pierce. (2004) Gaj. (2017) Arespacochaga et al. (2015)
Cryogenic condensation	Low operating temperature (5 ºC) Extremely low operating temperature (-70 ºC)	12-25 99.3	Low High	Medium High	• Easy to operate. • Highly effective technology.	• Extreme operating conditions: economically unfeasible unless high flow rates and high VMS concentrations are treated.	Shen et al. (2019) Ajhar et al. (2010) Arespacochaga et al. (2015)

Catalytic processes	Basic and acid oxides (CaO, MgO, Al_2O_3, SiO_2)	100 % (gradually decreasing to 9 % after 35 hours)	-	-	• Highly effective technology.	• Irreversible and rapid deactivation of the catalysts. • Operating temperatures: 200-400 ºC	Finocchio et al. (2008) Urban et al. (2009)
Membrane separation	Polydimethylsiloxane membranes	~ 80	High	Medium	• Simplicity and easy to operate. • Reduced volume systems.	• High investment and energy cost related to the compressors or vacuum pumps.	Ajhar et al. (2010) Basu et al. (2010) Shen et al. (2019) Arespacochaga et al. (2015)
Biological processes	Biotrickling filter, membrane bioreactors	70	Medium	Low	• Easy to operate. • Low operating costs. • Environmentally friendly.	• Limited by the low solubility of VMS • High operating gas residence times.	Pascual et al. (2020) Pascual et al. (2021) Santos-Clotas et al. (2020) Arespacochaga et al. (2015)

1.3 Biodegradation of siloxanes: a promising emergent alternative

1.3.1 Prokaryotes involved in siloxanes degradation

Biological processes are an attractive low-cost and environmentally friendly alternative to conventional physical-chemical technologies for the treatment of VMS. Biotechnologies for environmental remediation are based on the use of organic pollutants by microorganisms as energy and carbon source. In a biochemical reaction, microorganisms act as a catalyst to oxidize the organic pollutants (electron donor) by breaking their chemical bonds producing energy, while another compound is reduced (electron acceptor) (Lebrero et al., 2019). However, not all contaminants have been tested as biodegradable compounds. In the particular case of VMS, there have been some attempts to uncover if microorganisms are able to use siloxanes as carbon and energy source. However, the routes for the biological degradation of siloxanes by microorganisms still remain uncertain.

The first study that suggested the feasibility of the biological degradation of organosilicon compounds was conducted in 1967 by Fessenden and Fessenden (Fessenden and Fessenden, 1980). In this research, it was claimed that *Pseudomonas* species were likely able to degrade silane. Thereafter, different species of this genus have been reported as able to grow on complex organosiloxanes. Wasserbauer and Zadák (1990) proved the degradation of high molecular polydimethylsiloxane and low molecular weight siloxanes (i.e., L_4, L_3, L_2) using two species of *Pseudomonas* (*P. putida* and *P. fluorescens*) in the presence of O_2 (Wasserbauer and Zadak, 1990). Similarly, *P. aeruginosa* grew on oligo- and poly-organosiloxanes in the presence of glucose (Rościszewski et al., 1998). In both studies cell growth was observed, however, CO_2 evolution was not recorded and siloxane breakdown products were not identified.

Further on, Accetolla et al. (2008) studied the aerobic degradation of D4 as the only carbon source using three types of inocula: 1) a culture of *P. putida,* 2) activated sludge from an urban wastewater treatment plant, and 3) activated sludge from the wastewater treatment plant of a company producing silicones. The protein analysis and optical density measurements showed that *P. putida* didn't grow as a pure culture on D4 (Accettola et al., 2008). However, both enrichments from wastewater were able to grow using D4 as the only carbon source. In both cases, the predominant bacteria detected belonged to the genus *Pseudomonas,* being identified as *P. aeruginosa, P. putida* and *P. citronellosis* together with other genera with lower abundance (*Rhodanobacter, Zoogloea, Mesorhizobium, Xanthomonada*) (Figure 2).

Thus, the co-culture of different species seemed to be an important factor to obtain efficient D4 degradation. The main metabolite identified in this study was dimethylsilanediol (DMSD). Likewise, Li et al. (2014) observed aerobic degradation of D4 using an isolate of *P. aeruginosa* strain S240. L_3 (from DMSD) and trimethylmethoxysilane (from methanol) were detected, which indicated the presence of DMSD and methanol from the degradation of D4. Silicic acid and CO_2 were also recorded as degradation products. This last study proved that *P. aeruginosa* was able to use D4 as the only carbon source in the presence of O_2 (Li et al., 2014). The last study that pointed *Pseudomonas* as a siloxanes consumer was conducted by Boada et al. (2020), who isolated bacterial species using D4 as the sole carbon source in anaerobic conditions. Phylogenetic analysis revealed that the main isolate found belonged to the genus *Pseudomonas* (Boada et al., 2020).

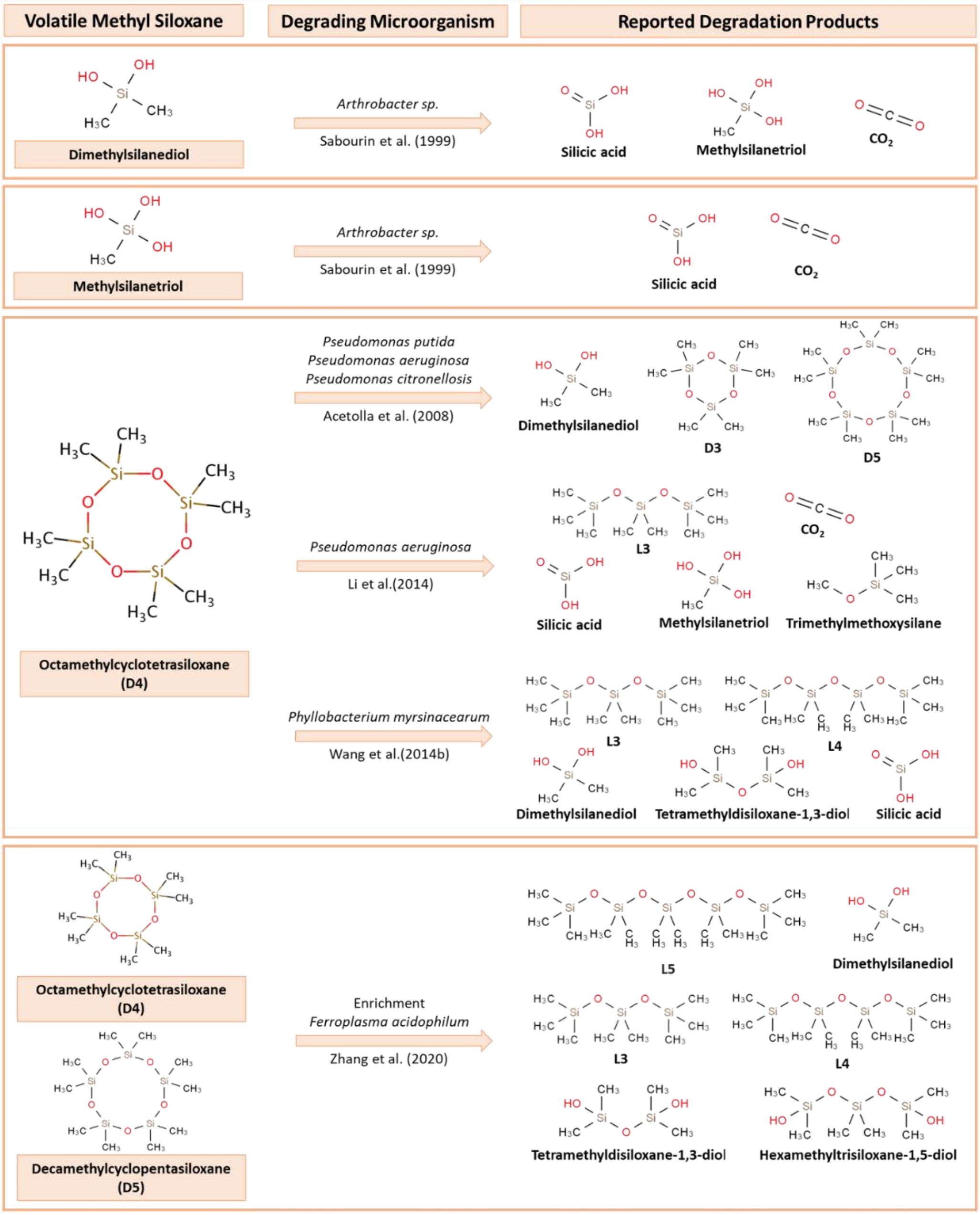


Figure 2. Structures of the biodegradation products, corresponding parent siloxanes and main prokaryotes reported to degrade siloxanes.

Pure strains from other genera different than *Pseudomonas* have been also identified as siloxanes degraders. Sabourin et al. (1996 and 1999) described biodegradation of DMSD and methylsilanetriol in the presence of oxygen and a primary carbon source by a new species of the genus *Arthrobacter*. In both studies, ^{14}C-DMSD degradation was linked to a small production of $^{14}CO_2$, ^{14}C-methylsilanetriol and inorganic silicate, while ^{14}C-methylsilanetriol degradation to $^{14}CO_2$ could not be proven (Lehmann et al., 1998; Sabourin et al., 1999). Members of *Phyllobacterium* were also linked to siloxanes degradation in aerobic conditions. In this research, the authors claimed that *Phyllobacterium myrsinacearum* in pure culture efficiently removed D4 during the operation of a biotrickling filter (BTF). Similar to Li et al. (2014), the authors identified in the liquid phase L_3, L_4, DMSD, and some small amounts of tetramethyldisiloxane-1,3-diol and silicic acid, potential by-products of D4 degradation (Wang et al., 2014b).

In recent studies of siloxanes biodegradation, advanced molecular tools such as next generation metagenomics, have been implemented to study the enriched population of siloxanes removal biotechnologies (Boada et al., 2021, 2020; Zhang et al., 2020). In these studies, sewage sludge was used as the inoculum for enrichment of organosiloxanes degraders. Interestingly, only Boada et al. (2020) identified *Pseudomonas* as one of the enriched genus after biodegradation of D4. However, the authors reported a new species of the genus *Methylibium* to be the most efficient D4 degrader. In a follow-up study, Boada et al. (2021) also identified the genus *Methylibium* as one of the most abundant genus in an anaerobic lab-scale biotrickling filter (Boada et al., 2021).

Alternatively, Zhang et al. (2020) enriched acidophilic microorganisms from anaerobic sludge during siloxanes treatment. In this study, the archaeal community was analyzed for the first time, exhibiting that the enriched population was highly dominated by the archaeal genus *Ferroplasma* (85.5 % relative abundance). The other main organisms found belonged to the genus *Acidithiobacillus* (9.5 %) and *Thermogymnomonas* (4.6 %) (Florentino et al., 2015). Degradation metabolites similar to those found by Li et al. (2014) and Wang et al. (2014b) were detected. More recently, Zhang et al. (2020) studied the degradation of siloxanes mixed with biogas, which contains CO_2, CH_4 and H_2S among other compounds. The authors related the growth of acidophilic prokaryotes with the use of carbon and energy sources different from VMS, and the removal of siloxanes with abiotic absorption by liquid recircularization in the biofilter, as well as adsorption onto the biomass (Zhang et al., 2020).

1.3.2 Biotechnologies for the removal of siloxanes

i. *Main bioreactor configurations tested to treat VMS*

As a growing number of studies try to disentangle the microbiology, the degradation products and the degradation pathways involved in biological siloxanes abatement, there has also been an increasing interest for the implementation of biotechnologies for the removal of these VMS (Urbaniec et al., 2020). In this sense, the feasibility of continuously abating these pollutants from biogas has been tested in different bioreactor configurations, including bioscrubbers, biofilters and biotrickling filters (Shen et al., 2018). Despite the significant advances made in the past years, the highest VMS removal efficiency reported to date in a biological reactor has been ~ 74 % at an empty bed residence time (EBRT) of 13.2 min (Li et al., 2014), lower than the removals achieved in physical-chemical technologies. This has triggered additional efforts to boost the performance of biological alternatives.

The most investigated and best performing bioreactor configuration has been biotrickling filtration (Figure 3.a). Biotrickling filters are considered the optimum technology to treat low and variable-concentration polluted streams. In this configuration, the VMS-laden biomethane passes through a packed bed of synthetic inert material where microbial communities responsible for VSM biodegradation are immobilized as a biofilm. The pollutants are firstly transferred to the aqueous phase and subsequently absorbed/adsorbed in the biofilm where they are biodegraded by the microbial community (Urbaniec et al., 2020). A continuous recirculation of a trickling liquid solution prevents drying of the biofilm, provides nutrients for microbial growth and washes-out from the biofilm any potential inhibitory metabolite produced during VSM biodegradation (Xue et al., 2013).

Early research focused on abatement of the cyclic VMS, D3 and D4, in both aerobic and anoxic BTFs. The maximum RE achieved for D3 was low, around 20% for an EBRT of 3.5 s (Accettola et al., 2008). However, a higher removal efficiency of 43% was achieved for D4 when the EBRT was increased to 19.5 min (Popat and Deshusses, 2008). These results suggested that the low removals of VMS derived from their low mass transfer rates from the gas phase to the liquid phase and the reduced EBRTs. Higher D4 removals (~55 %) were achieved in an aerobic BTF inoculated with activated sludge obtained from the effluent of an organic silicon manufacturer operated at EBRTs between 12 and 30 min (Wang et al., 2014a). The reinoculation of the same BTF with a previously isolated microorganism (*Phyllobacterium myrsinacearum*) resulted in a slight increase in the removal performance up to 60.2 % at an EBRT of 24 min (Wang et al., 2014b). Both studies demonstrated a detrimental effect on the system performance when decreasing the EBRT, with optimum values ranging from 15 to 24 min and a pH of the recycling liquid between 4 and 7. Some researchers have recently investigated the simultaneous removal of VMS and trace compounds such as H_2S, hexane, toluene and/or limonene (Boada et al., 2021; Zhang et al., 2020), reaching maximum removal efficiencies of D4 and D5 between 40 and 50 %.

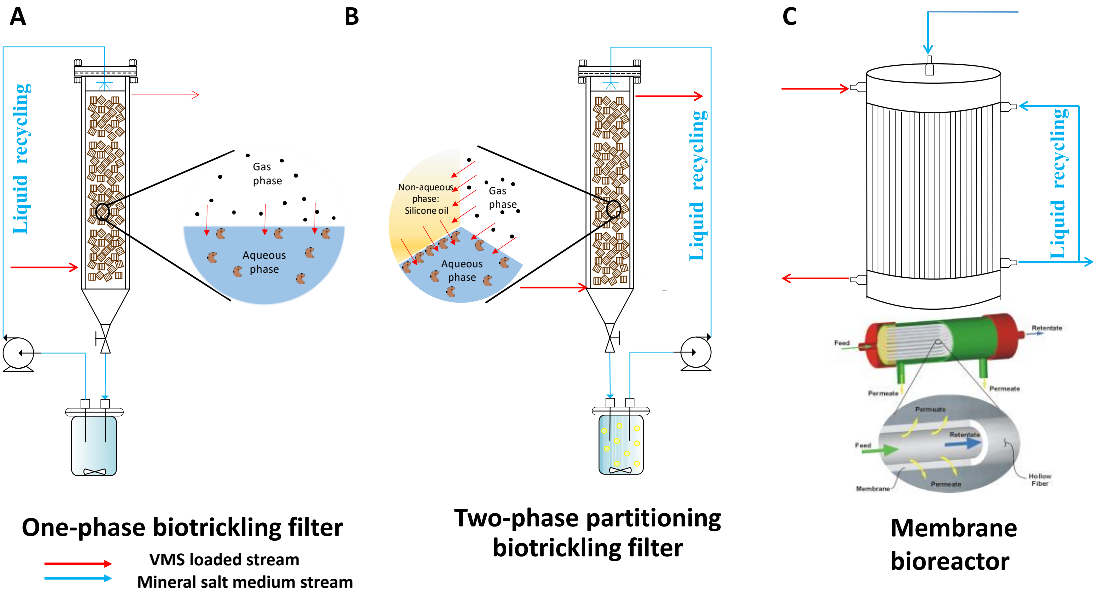
The limited performance reported for siloxanes biodegradation in BTFs has been associated to the low solubility of siloxanes in the recycling aqueous mineral medium (high dimensionless Henry's law coefficient (Equation 2); L2: 404, L3: 1440, D3: 72, D4: 252; D5: 183 (www.henrys-law.org)), which hinders the mass transfer of these hydrophobic compounds from the gas phase to the aqueous phase and consequently, reduces their availability to the microbial community.

$$H_{G/L} = \frac{C_G}{C_L^*} \qquad \textbf{Equation 2}$$

Where C_L* is the pollutant concentration in the interphase in equilibrium with the pollutant concentrations in the gas phase (C_G).

This entails operation at high EBRTs in order to promote an effective gas-liquid mass transfer, resulting in increased bioreactor volumes and, therefore, higher investment costs. In this sense, an enhancement of D4 removal to 74% at an EBRT of 13.2 min was observed in a biotrickling filter inoculated with *Pseudomonas aeruginosa S240*. This was associated to the presence of rhamnolipids, organic biosurfactants produced by the genus *Pseudomonas* which boosted the mass transfer of D4, as proved by the partitioning test performed by the authors: the gas/liquid partitioning coefficient was up to 7 times lower in the aqueous solution containing rhamnolipids (Li et al., 2014). Another strategy recently implemented to improve the mass transfer of VMS has been the addition of high-capacity adsorbents to the packing material (i.e. activated carbon), resulting in an increase of D5 removal from 16 to 45% (Santos-Clotas et al., 2019).

Hollow fiber membrane bioreactors (MBRs) (Figure 3.c) constitutes another novel technology lately implemented for the removal of VMS along with other trace compounds. MBRs rely on the separation of the VMS-polluted stream, which circulates on the dry side of the membrane, from the liquid solution, which circulates on the wet-side where the biofilm grows attached to the membrane surface. This configuration improves the mass transfer of VMS, since the VMS selectively permeate the membrane and reach the biofilm without being in contact with the aqueous phase. Moreover, MBRs ensure an optimal moisture and nutrient content in the biofilm. However, they entail high investment costs, and membrane clogging associated with biofilm overgrowth can increase operating costs (Kumar et al., 2008). To date, the only authors testing this configuration for siloxanes abatement have reported removals for D4 and D5 of ~17 and ~21 % (Santos-Clotas et al., 2020). Further research on membrane materials that support an increased mass transfer of the gaseous compounds to the microbial biofilm is necessary in order to ensure the cost-efficiency of this novel biotechnology.



One-phase biotrickling filter

Two-phase partitioning biotrickling filter

Membrane bioreactor

Figure 3. Schematic representation of biological technologies: a) single phase biotrickling filter (BTF) and b) two-phase partitioning biotrickling filter (TP-BTF).

The low investment and operating costs of biotechnologies compared to commercial physical-chemical processes (Table 2), along with the promising results recently obtained, highlight the potential of biological processes as a promising alternative for the removal of VMS from biogas. However, mass transfer improvement strategies should be engineered in order to further optimize VMS abatement biotechnologies.

ii. *Innovative mass transfer strategies*

The feasibility of implementing siloxane biodegradation technologies at industrial scale relies on the engineering and scale up of high mass transfer bioreactors. To this end, novel strategies and modifications of the configuration of conventional bioreactors have been evaluated.

Two-phase partitioning bioreactors

In 2008, Popat and Deshusses (2008) suggested that the mass transfer limitation in bioreactors aimed at siloxanes removal might be overcome by adding a biocompatible non-aqueous phase, such as silicone oil or oleyl alcohol, to the recycling liquid in BTF. This innovative configuration, named two-phase partitioning bioreactor (TPPB) (Figure 3.b), is based on the addition to conventional bioreactors of a non-aqueous liquid phase (NAP) with high affinity for the target gas pollutants. The NAP increases the mass transfer of the hydrophobic compounds from the gas phase to the biofilm (Lebrero et al., 2019). The volumetric pollutant mass transfer rate (g m^{-3} h^{-1}) is determined by Equation. 3:

$$F_{G/L} = K_L^{G/L} a \left(\frac{C_G}{H_{G/L}} - C_L \right) \qquad \textbf{Equation 3}$$

Where $F_{G/L}$ represents the volumetric pollutant mass transfer rate (g m^{-3} h^{-1}), $K_L^{G/L}a$ is the overall volumetric mass transfer coefficient (h^{-1}), C_G and C_L are the pollutant concentrations (g m^{-3}) in the gas and liquid phase, respectively, and $H_{G/L}$ the dimensionless Henry’s law constant for the target gas pollutant (Equation 2).

If the liquid phase consists of an aqueous solution, the volumetric mass transfer rate of a hydrophobic pollutant significantly decreases since the gas/liquid partitioning coefficient ($H_{G/L}$) is up to 6 orders of magnitude higher compared to that of soluble contaminants

(Kochetkov et al., 2001; Surita and Tansel, 2014), which decreases the concentration gradient between the gas and liquid phases.

Adding an organic solvent as a NAP creates a new and effective mass transport route for hydrophobic pollutants such as siloxanes (Figure 4). The partition coefficient air/non-aqueous phase is considerably lower for hydrophobic compounds. In the case of silicone oil, the partitioning coefficient of siloxanes is up to 4000 times lower compared to that of air/water (Patel et al., 2017). The presence of this non-aqueous phase increases the solubility of hydrophobic pollutants, the driving forces and the interfacial area, thus resulting in an enhancement of their global gas-microorganisms mass transfer (Muñoz et al., 2014). Moreover, recent research has proved the ability of microorganisms to consume contaminants directly from the NAP, therefore the final volumetric mass transport rate would be the combination of both gas/aqueous phase and gas/NAP transports (Cantera et al., 2016; Hernández et al., 2012).

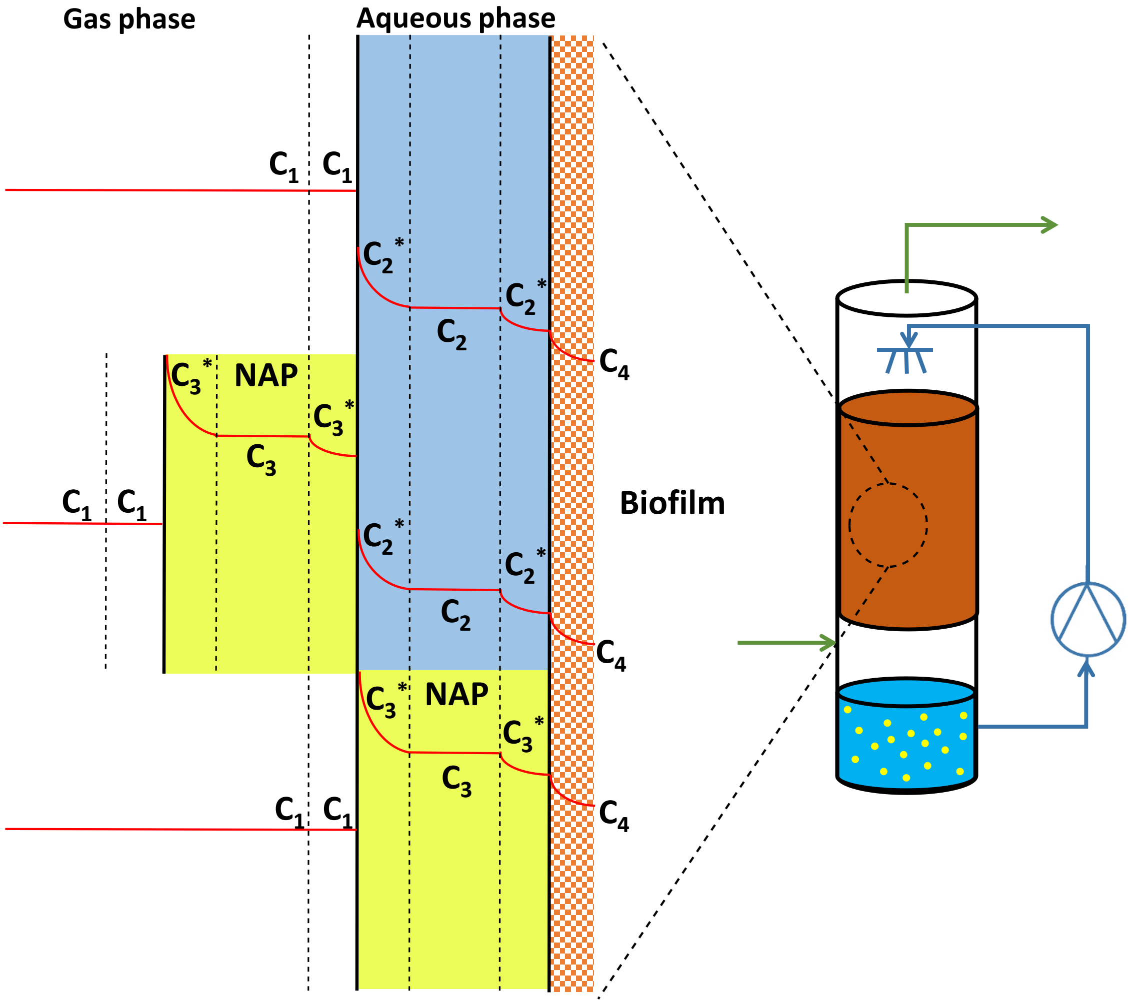


Figure 4. Pollutant concentration (C) profiles in a two-phase partitioning BTF during its mass transfer from the gas to the liquid phase: different transport routes (gas (1), aqueous (2), and non-aqueous (3) phases and biofilm (4)).

In addition, the NAP reduces the possible toxic effects of pollutants or secondary metabolites to the microbial community (Muñoz et al., 2012), and acts as carbon source reservoir for the microorganisms during famine or low-concentration periods. This strategy has been successfully implemented for the degradation of other hydrophobic contaminants including hexane, styrene or toluene, obtaining high pollutant removal performances.

The addition of a NAP has been successfully tested in different bioreactor configurations. The most common TPPB configuration for the removal of air pollutants has been the continuous stirred tank reactor (CSTR) (Figure 5.a). In this system, the gas is sparged in the mechanically stirred culture broth with the microorganisms suspended. However, the high energy consumption associated to the agitation and the dispersion of the organic and gas phase has promoted the investigation of new TPPB configurations (Arriaga and Aizpuru, 2019).

For instance, airlift bioreactors (ALBs) avoid the high energy consumptions of CSTR thanks to their pneumatical recirculation system. ALBs are cylindrical bubble column bioreactors divided into different chambers connected at the top and at the bottom of the column. The polluted gas stream diffuses through one of the chambers (sparger zone) creating a liquid circulation between the chambers due to the different gas hold-up (Figure 5.b). Recent studies have demonstrated the superior removal performance of complex organic compounds such as BTEX, ethyl acetate, and dichloromethane in two-phase partitioning ALBs compared to a conventional single-phase airlifts (Lebrero et al., 2019).

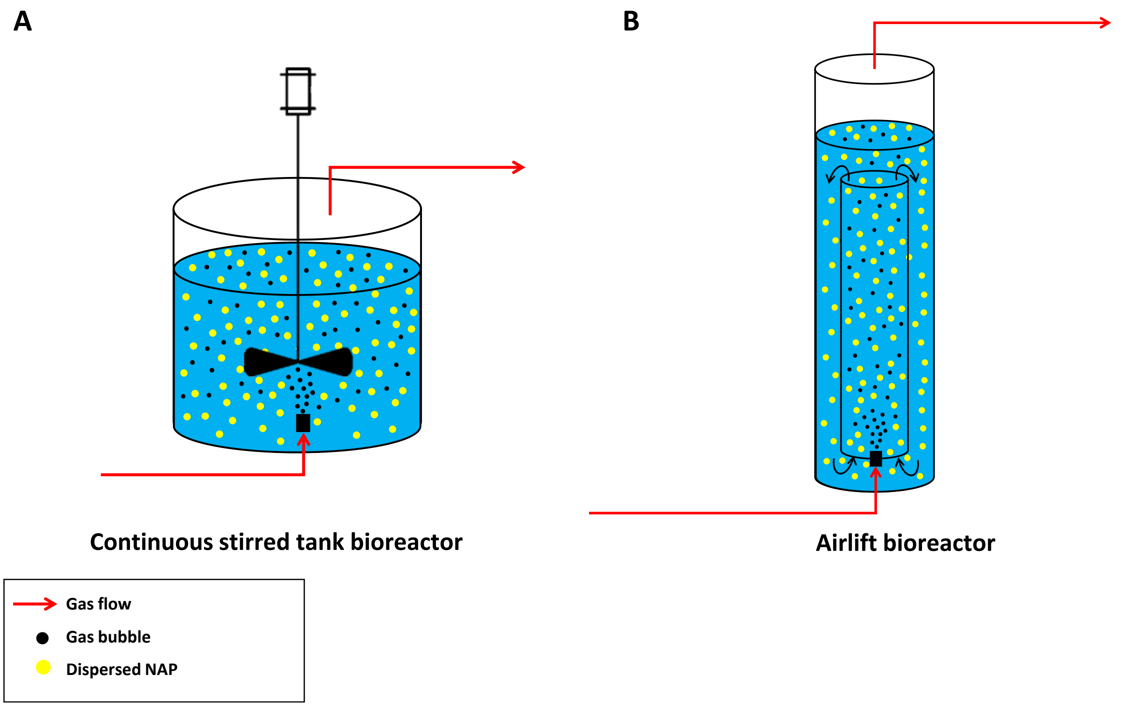


Figure 5. Schematic representation of two-phase partitioning a) continuous stirred tank bioreactor (CSTR) and b) airlift bioreactor (ALB).

Finally, two-phase partitioning BTFs (TP-BTF) have been also assessed as an alternative to conventional BTFs to enhance the removal of poorly soluble gas pollutants (Figure 3b). The trickling solution in this configuration consists of a nutrient aqueous solution homogenously mixed with the NAP (Quijano et al., 2009). The addition of the NAP to the conventional BTFs is an excellent strategy to overcome the mass transfer limitation of hydrophobic pollutants in this system, associated to the continuous presence of an aqueous layer covering the biofilm. TP-BTFs have been widely implemented for the treatment of hydrophobic VOCs, such as styrene, α-pinene and toluene, and also of CH_4. In general, an improved performance of the TP-BTFs compared with conventional BTFs has been demonstrated in previous research (Lebrero et al., 2019). The elimination capacities achieved increased by ~60% for styrene (Zamir et al., 2015) and by ~130% for CH_4 (Rocha-Rios et al., 2009) in the two-phase configuration.

The selection of the NAP and the NAP/aqueous phase ratio are critical operation parameters in TPPBs to optimize their performance. Silicone oil is the NAP most commonly employed due to its favourable characteristics such as non-degradability, biocompatibility, high affinity and selectivity, low volatility, low cost and chemical and thermal stability (Lebrero et al., 2019). In general, higher NAP/aqueous phase ratios increase both the affinity of the liquid mixture for the VOC and the time necessary to reach thermodynamic equilibrium (Parnian et al., 2016), thus enhancing the global mass transfer volumetric ratio. Previous studies observed the improvement of CH_4 abatement when the silicone oil ratio increased from 5 to 10% in a CSTR (Rocha-Rios et al., 2011). According to Equation 3, higher ratios allow for an increase in the interfacial area involved in gas-liquid mass transport, thus improving the mass transfer of siloxanes from the gas phase to the liquid phase. However, the amount of NAP present in the liquid mixture could negatively impact other operation parameters, such in the case of TP-BTFs where higher NAP ratios could trigger deterioration of the packing media, thus reducing the overall performance of the system (Lebrero et al., 2019). As observed by Lebrero et al. (2014), an increase in the silicone oil ratio from 10 to 20% decreased the performance of a TP-BTF for hexane removal, which was associated to the lower water holding capacity of the packing bed and channelling of the gas flow (Lebrero et al., 2014).

To the best of the authors knowledge, this technology has not been previously applied for siloxanes abatement. However, the high affinity of VMS for the silicone oil and the promising results reported by previous studies focused on TP-BTFs for multiple hydrophobic VOCs, open up a new research pathway for purification of VMS-laden air and biogas.

Operational modifications: trickling liquid velocity and internal gas recycling.

In order to enhance the mass transfer of VOCs and poorly soluble gases in conventional bioreactors, different operational strategies have been tackled in the last decade. In the particular case of BTFs, optimizing the trickling liquid velocity (TLV) or implementing an internal gas recirculation have been studied as potential solutions (Figure 6), among others.

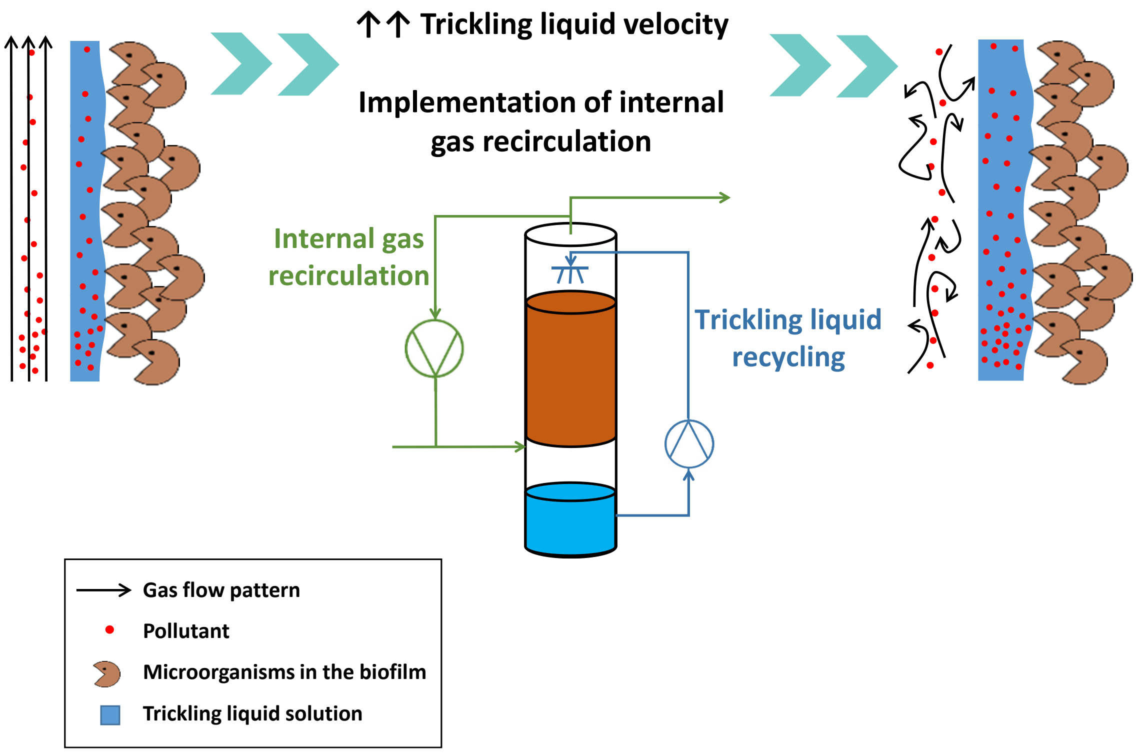


Figure 6. Operational modifications in a BTF: influence of the trickling liquid velocity and internal gas recirculation on the pollutant transfer and gas flow pattern.

Previous research has defined TLV as a critical parameter governing the gas-liquid mass transfer in a BTF, with typical values ranging from 1.1 to 20 (Cano et al., 2019). The influence of the TLV in the overall mass transfer coefficient ($K_L^{G/L}a$, Equation 3) was studied with 11 different packaging materials, concluding that the $K_L^{G/L}a$ value increased with the TLV regardless of the packing material (Liu et al., 2015). In addition, high TLVs increase the nutrient availability to the biofilm as a result of the higher wet packed bed area (Cano et al., 2019). Caicedo et al. 2018 observed REs 3 times higher in the toluene and ethylbenzene abatement when the TLV was increased from 2 to 10 m h^{-1}. This effect was observed in random and structured polyurethane foam, and was even more noticeable with the best performing material (structured polyurethane foam) (Caicedo et al., 2018). In addition to the enhancement produced in the gas–liquid mass transport, the authors observed an increase in the biofilm colonization of the polyurethane foam induced by the improved wettability of the packed bed. Similar effect was observed for sulphur compounds (such as hydrogen sulphide, methyl mercaptan, dimethyl disulphide and dimethyl sulphide), increasing their RE up to 2.9 times when the TLV was raised from 0.3 to 1.2 m h^{-1} (Jia et al., 2020). Moreover, the increase in the TLV raised the dissolved oxygen concentration in the case of aerobic BTFs, consequently increasing the degradation of the target pollutant (López et al., 2016). However, a further increase in the TLV to 3 m h^{-1} did not affect to the removal of these pollutants. On the contrary, a reduction in the removal of H_2S was recorded at high TLV values in a BTF packed with polypropylene pall rings, an effect associated to biofilm detachment (Bu et al., 2021). However, this parameter must be optimized in order to avoid negative impacts on the system performance and excessive operating costs.

Internal gas recirculation is an innovative mass transfer strategy that reduces the mass transfer resistance and decouples the gas–liquid turbulence inside the reactor from the actual gas residence time (Estrada et al., 2014). This strategy has been recently implemented in different bioreactor configurations. In a conventional BTF for CH_4 removal, a 2.5-fold elimination capacity increase was achieved when an internal gas recirculation of 18 L min^{-1} was implemented (Estrada et al., 2014). Similarly, Rodriguez et al. (2020) reached CH_4 ECs 4 times higher when the gas recirculation was implemented in a bubble column bioreactor (Rodríguez et al., 2020). The positive effect of increasing the gas recirculation rate in an ALB for CH_4 abatement on the mass transfer enhancement capacity was also corroborated by Rocha-Rios et al., who reported an increased system performance of 51% by increasing the ratio from 0.5 to 1 volumes per minute (vvm) (Rocha-Rios et al., 2011).

Similar to TPPBs, the influence of these strategies on siloxane removal performance has not been studied to date. Thus, both operational modifications could represent a promising strategy to enhance the removal of siloxanes in conventional bioreactors.

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Chapter 2.

Aim and scope of the thesis

2.1 Justification of the thesis

Volatile methyl siloxanes (VMS) are organosilicon compounds increasingly used in several industrial applications due to their excellent properties such as low aqueous solubility, high compressibility, low flammability, low surface tension, water repelling properties and high thermal stability. In fact, the application of VMS in consumer products has exponentially increased during the last decade, and products made with VMS are expected to grow by 78% during the next 25 years. As a result of their volatile nature, end-use VMS are discharged to the atmosphere, or accumulated in landfills and wastewater treatment plants where they end up in the biogas produced at such facilities. These VMS disposed in the environment have potentially toxic effects in animals, especially in mammals, derived from their bioaccumulation that negatively affects the respiratory tract and reproductive system. Moreover, VMS also have negative economic impacts caused by their oxidation into crystalline SiO_2 deposits during biogas combustion, which damage the equipment and decrease the efficiency of the subsequent biogas valorisation as a renewable energy source. Therefore, the effective removal of siloxanes from gaseous emissions is of utmost importance. Biotechnologies represent a low-cost and environmentally friendly alternative for the control and removal of VMS from gas emissions. However, the abatement of VMS with bioprocesses is still restricted by two main aspects:

i) The low solubility of siloxanes in the aqueous phase where microorganisms bio-catalyse their degradation. This reduces the gas-liquid mass transfer of VMS and therefore, their availability for the microorganisms involved in their degradation.

ii) The limited understanding about the VMS biological catabolism: the microorganisms, genes and metabolisms involved in the processes are still unknown.

2.2 Main objectives

The overall objective of this research was the development and optimization of biological technologies for siloxanes removal as a sustainable and environmentally friendly solution to treat siloxanes from biogas and environmental emissions. Due to the low solubility of VMS in the aqueous phase, this objective was addressed by designing and implementing new bioreactor configurations that boosted the mass transport of VMS to the siloxane-degrading microorganisms. Special attention was given to the microbial population underlying the process and the metabolic mechanisms involved in siloxanes degradation. More specifically, the specific objectives pursued were:

i. Assessment of the feasibility, in terms of VMS removal performance, of a high mass transfer two-phase partitioning biotrickling filter (TP-BTF) in comparison to conventional BTF.

ii. Optimization of key operational parameters, such as the empty bed resident time and the silicone oil fraction, that could improve VMS degradation under aerobic and anoxic conditions.

iii. Evaluation of the potential of novel mass transfer strategies for the removal of VMS, such as the increase in the recycling liquid velocity and the implementation of an internal gas recirculation.

iv. Appraisal of the microbial community involved in the biological degradation of VMS.

v. Upscaling of the process in a pilot semi-industrial bioreactor (TLR 3-6) to test the efficiency of the new technology as a polishing step for biogas upgrading.

vi. Assessment of the techno-economic and environmental advantages of biotechnologies in comparison to physical-chemical technologies.

2.3 Thesis outline

In the present thesis, the enhancement of siloxanes abatement from gaseous emissions in TP-BTFs was investigated and compared to the removals obtained in conventional biotechnologies.

First, a comparative evaluation of a TP-BTF and a conventional BTF was carried out in **Chapter 3** in order to fulfil objective I. According to objective II, the influence of the EBRT and the percentage of the organic fraction in the trickling solution was optimized to enhance VMS removals in TP-BTF in **Chapter 4**. In order to study the application of this system during biogas purification, which occurs in the absence of O_2, the TP-BTF was implemented under anoxic conditions at the optimum operating parameters obtained in Chapter 3 and 4 (**Chapter 5**). This fulfilled objective II. With the promising results obtained, the influence of innovative mass transfer strategies, such as the influence of the recycling liquid velocity and the implementation of an internal gas, was studied in the TP-BTF under both aerobic and anoxic conditions according to the objective III (**Chapter 6**). Moreover, the influence of the inlet VMS concentration was tested by operating the TP-BTF at high (**Chapters 3 and 4**) and low (**Chapters 5 and 6**) concentrations. The specialized microbial community developed throughout this research was also studied in order to fulfil objective IV (**Chapters 3, 4, 5 and 6**).

In **Chapter 7**, a techno-economic and environmental assessment was carried out in order to compare the biological technologies, especially the BTF, with the most common physical-chemical technologies available in the market according to objective VI.

Finally, the TP-BTF was scaled up from TLR 3 to 6 in the Waste Technological Innovation Center “Alfonso Maíllo” (CIAM, URBASER) aimed at treating the biomethane obtained from a photosynthetic biogas upgrading unit (**Chapter 8**) fulfilling objective V.

Chapter 3.

Comparative assessment of two biotrickling filters for siloxanes removal: Effect of the addition of an organic phase

This chapter was adapted after its publication in *Chemosphere:*

Pascual, C., Cantera, S., Muñoz, R., Lebrero, R., 2020. Comparative assessment of two biotrickling filters for siloxanes removal: Effect of the addition of an organic phase. Chemosphere 251, 126359. https://doi.org/10.1016/j.chemosphere.2020.126359

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Chapter 4.

Siloxanes removal in a two-phase partitioning biotrickling filter: Influence of the EBRT and the organic phase

https://doi.org/10.1016/j.renene.2021.05.144

This chapter was adapted after its publication in *Renewable Energy:*

Pascual, C., Cantera, S., Muñoz, R., Lebrero, R., 2021. Siloxanes removal in a two-phase partitioning biotrickling filter: influence of the EBRT and the organic phase. Renew. Energy 177. https://doi.org/10.1016/j.renene.2021.05.144

Chapter 5.

Innovative polishing stage in biogas upgrading: Siloxanes abatement in an anoxic two-phase partitioning biotrickling filter

This chapter was adapted after its publication in *Journal of Cleaner Production:*

Pascual, C., Cantera, S., Muñoz, R., Lebrero, R., 2022. Innovative polishing stage in biogas upgrading: Siloxanes abatement in an anoxic two-phase partitioning biotrickling filter. J. Clean. Prod. 371. https://doi.org/10.1016/j.jclepro.2022.133427

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Chapter 6.

Assessment of the mass transfer strategy and the role of the active bacterial population on the biological degradation of siloxanes

This chapter was adapted after its submission in *Fuel*.
The manuscript of this chapter is currently under review.

Assessment of the mass transfer strategy and the role of the active bacterial population on the biological degradation of siloxanes

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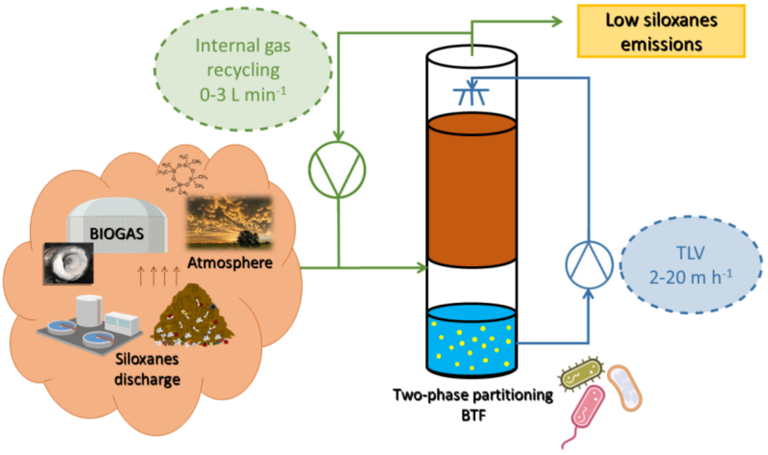
Highlights

- Anoxic and aerobic VMS abatement was tested in a two-phase partitioning BTF
- Liquid and gas recirculation were optimized as mass transfer enhancement strategies
- Total VMS removal (47-55%) was recorded for TLV of 10 m h^{-1}, without gas recycling
- Highest removal was recorded for D5 (75%) under both anoxic and aerobic conditions
- Active bacteria involved in VMS degradation were studied through RNA sequencing

Abstract

Upgrading of biogas to remove siloxanes is mandatory to meet the standards required for its use as a substitute of fossil fuels. The biological degradation of these pollutants is a low cost and environmental friendly alternative to conventional techniques, albeit certain limitations, such as the low solubility of siloxanes, still hinder its application. In the present work, two parameters were optimized in aerobic and anoxic two-phase biotrickling filters (TP-BTF): the trickling liquid velocity (TLV) and the internal gas recirculation, with the aim of improving siloxanes biological removal. The results obtained showed that the increase in TLV from 2 to 10 m h^{-1} resulted in higher removal efficiency (RE) under both anoxic and aerobic conditions, reaching maximum values of 55 and 47%, respectively. This effect was more significant for the linear siloxanes. On the contrary, a further increase in the TLV to 20 m h^{-1} together with the implementation of internal gas recirculation caused an excessive turbulence in the liquid side, detaching the biofilm and having a negative effect for the RE. The cyclic siloxanes were more effectively eliminated along the process (maximum REs of 75% were recorded for decamethylcyclopentasiloxane (D5)), but the studied system modifications exerted a minor effect on their RE. The active bacterial population involved in siloxanes degradation (studied throughout RNA extraction and sequencing) was dominated by the clade *Acidithiobacillacea KCM-B-112* and the genus *Parvibaculum* in aerobic conditions, while the members of the family *Phyllobacteriacea* and the genera *Nocardia* and *Baekduia* dominated in anoxic conditions.

Keywords: Biogas upgrading, Biotrickling filter, Silicone oil, Two-phase partitioning bioreactor, VMS removal.



6.1. Introduction

Improving energy efficiency and reducing primary energy sources, including nuclear energy, are some of the biggest policy concerns around the world. According to the EU 2030 climate & energy framework, a 32% share of renewable energy is targeted by 2030 (European Commission, 2018). Within this context, biogas constitutes one of the most promising candidates among the different renewable sources (Lisowyj and Wright, 2020). However, the residual gaseous compounds present in biogas should be removed in order to increase its energy efficiency and to avoid operational problems and negative health/environmental impacts. Among them, volatile methyl siloxanes (VMS) are some of the most problematic biogas contaminants, since they damage biogas engines and equipment (abrasion caused by silica particles formed during biogas combustion) raising the operating costs and reducing the efficiency of energy generation facilities. For this reason, there is a concentration limit of siloxanes in raw biogas that depends on its subsequent use. In European legislation, the limit for the injection of biomethane into natural gas grids and for its use as vehicle fuel is set at ~1 mg Si m^{-3} (Standardization, 2016).

Commercial physical-chemical technologies mainly based on adsorption, absorption and condensation processes, have demonstrated high VMS removal efficiencies, complying with existing standards. However, their environmental impact together with their excessive operating costs have promoted the development of sustainable alternatives based on biological processes (Pascual et al., 2022b). The most studied bioreactor configurations in the field of VMS abatement, under both aerobic and anoxic conditions, are biotrickling filters (BTFs) (Shen et al., 2018). Previous research has identified the poor gas-liquid mass transfer of VMS, associated to their low solubility, as the major limitation during their biological degradation. The optimization of bioreactors to boost mass transfer of poorly soluble pollutants has been widely investigated. Mixing the packing material with activated carbon (Santos-Clotas et al., 2019) or adding an organic phase to the recycling liquid (in the so called two-phase partitioning BTF, TP-BTF) (Pascual et al., 2020) have been studied as strategies to improve mass transfer of VMS with satisfactory results.

Apart from these solutions, optimization of some operating parameters such as the trickling liquid velocity (TLV) or the internal gas recirculation might lead to an enhanced performance as they determine the mass transfer of pollutants from the gas to the liquid phase. Several studies have assessed the effect of the TLV on the global mass transfer coefficient for the removal of H_2S, methane and other VOCs (Bu et al., 2021; Caicedo et al., 2018; Estrada et al., 2014). The results concluded that the TLV increases the transport of the target pollutant from the gas phase to the trickling solution, while promoting the growth of biomass in the packing material. On the other hand, the implementation of an internal gas recirculation has been proven as an outstanding mass transfer strategy in submerged culture systems. Bubble column bioreactors with internal gas recirculation operated to remove CH_4 or H_2, exhibited an increased turbulence and global mass transfer coefficient (Bassani et al., 2017; Rocha-Rios et al., 2011; Rodríguez et al., 2020).

The present work aimed at testing in a lab-scale TP-BTF the influence of the TLV and the internal gas recirculation in the degradation of VMS under both anoxic and aerobic conditions. The model VMS tested were those commonly found in biogas: hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5). Furthermore, the specialization of the active bacterial population was analyzed throughout RNA sequencing, which allowed to identify the main active bacteria involved in VMS degradation.

6.2. Materials and Methods

6.2.1. Mineral salt medium and inocula preparation

The mineral salt medium (MSM) was composed of (g L^{-1}): KH_2PO_4, 0.7; $K_2HPO_4 \cdot 3H_2O$, 0.917; KNO_3, 3; NaCl, 0.2; $MgSO_4 \cdot 7H_2O$, 0.345; $CaCl_2 \cdot 2H_2O$, 0.026; and 2 mL L^{-1} of a micronutrient solution containing (g L^{-1}): EDTA, 0.5; $FeSO_4 \cdot 7H_2O$, 0.2; $ZnSO_4 \cdot 7H_2O$, 0.01; $MnCl_2 \cdot 4H_2O$, 0.003; H_3BO_3, 0.003; $CoCl_2 \cdot 6H_2O$, 0.02; $CuCl_2 \cdot 2H_2O$, 0.001; $NiCl_2 \cdot 6H_2O$, 0.002; $NaMoO_4 \cdot 2H_2O$, 0.003. All chemicals used for the preparation of the MSM were purchased from Panreac (Barcelona, Spain). L2 (98.5% purity), L3 (98 % purity), D4 (98 % purity) and D5 (97 % purity) were obtained from Sigma Aldrich (San Luis, USA). The experiments were carried out using consortia enriched from activated sludge of previous TP-BTFs treating siloxanes under anoxic (Pascual et al., 2022a) and aerobic (Pascual et al., 2021) conditions. The aerobic consortium was enriched in a TP-BTF fed with a VMS mixture (L2, L3, D4 and D5) as the solely carbon and energy source at concentrations ≈ 800 mg m^{-3} for 124 days, while the anaerobic consortium was enriched in an anoxic TP-BTF fed with a VMS mixture (L2, L3, D4 and D5) as the sole carbon and energy source at a concentration ranging between 100 and 250 mg m^{-3} for 126 days.

6.2.2. Experimental setup and operating procedure

The experimental systems (Figure 6.1) consisted of two identical cylindrical PVC columns (8.4 cm diameter, 37.5 cm height) with a working volume of 2 L, packed with Kaldnes K1 Micro rings (Evolution Aqua, UK). The BTFs were inoculated with the anoxic and aerobic enriched cultures obtained as described in previous section 6.2.1.

The synthetic VMS-loaded inlet stream was prepared by injecting a liquid mixture containing L2, L3, D4 and D5 with a syringe pump (Fusion 100, Chemyx Inc., USA) into an air (aerobic BTF) or a N_2 (anoxic BTF) stream of 33 mL min^{-1} controlled by means of a rotameter. The VMS-loaded stream entered a mixing chamber to promote VMS volatilization and homogenization prior feeding at the bottom of the corresponding column. Inlet and outlet VMS and CO_2 concentrations in the gas phase were periodically measured with Gastight™ SampleLock™ syringes (Agilent, Santa Clara, California, USA) of 500 and 100 µL, respectively (Figure 6.1).

The MSM-silicone oil liquid mixture (70/30 % v/v) was recycled by a peristaltic pump (Watson-Marlow 313D) from an external 1-L holding tank magnetically stirred at 300 rpm. This liquid mixture was continuously recycled to the top of the column countercurrently with the VMS-loaded stream.

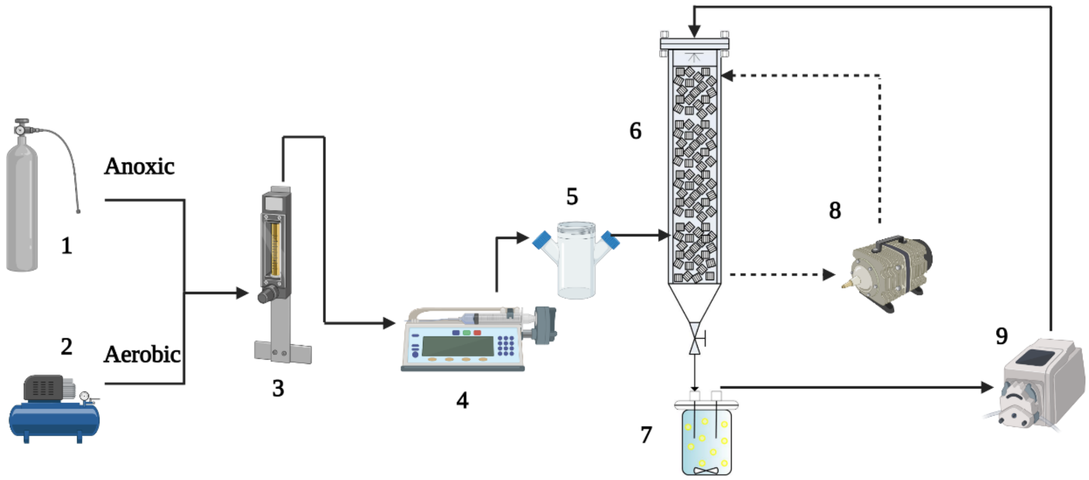


Figure 6.1. Schematic representation of the experimental set-up. (1) N_2 cylinder, (2) air compressor, (3) rotameter, (4) syringe pump, (5) mixing chamber, (6) biotrickling filter, (7) liquid mixture reservoir, (8) internal gas recirculation pump and (9) liquid recycling pump.

An abiotic test was initially performed for 27 days to discard the possibility of siloxanes removal and to ensure that there was no biological activity in the system prior to inoculation. For this purpose, the test was initiated with the empty PVC column, while sterile packing material and MSM were added in subsequent steps.

The anoxic and aerobic systems were operated for 140 (Table 6.1) and 177 (Table 6.2) days, respectively, in two different test series devoted to assess (i) the influence of the TLV (S1-S4) and (ii) the effect of the internal gas recirculation (S5 and S6).

The BTFs were operated at an empty bed residence time of 1 h and a periodical replacement of 300 mL of the culture broth with fresh MSM every seven days (equivalent to a hydraulic retention time of 47 days) throughout the entire experiment. The pH and total organic carbon (TOC), inorganic carbon (IC), total nitrogen (TN), total silicon (Si), nitrite and nitrate concentrations were analyzed in the cultivation broth withdrawn.

Table 6.1. Experimental conditions tested in the anoxic TP-BTF.

	Time course (days)	**VMS inlet concentration (mg m^{-3})**	**TLV (m h^{-1})**	**Internal gas recirculation (L min^{-1})**
S1	0 - 26	178 ± 20	2	-
S2	27 - 42	204 ± 25	10	-
S3	43- 70	213 ± 10	20	-
S4	71 - 96	202 ± 18	10	-
S5	97-116	247 ± 14	10	1
S6	117-140	243 ± 11	10	3

Table 6.2. Experimental conditions tested in the aerobic TP-BTF.

	Time course (days)	**VMS inlet concentration (mg m^{-3})**	**TLV (m h^{-1})**	**Internal gas recirculation (L min^{-1})**
S1	0 - 33	237 ± 12	2	-
S2	34 - 72	278 ± 11	10	-
S3	73 - 100	273 ± 22	20	-
S4	101 - 142	312 ± 24	10	-
S5	143 - 163	295 ± 21	10	1
S6	164 - 177	279 ± 4	10	3

The VMS-loaded streams were maintained at concentrations between 200 and 300 mg m^{-3}. The trickling liquid solution was progressively increased during the experimental test series from 2 m h^{-1} in S1 to 10 and 20 m h^{-1} in stages S2 and S3, respectively. Finally, the TLV was reduced again to 10 m h^{-1} and maintained at this value during the rest of the experiment. Internal gas recirculation was implemented at 1 and 3 L min^{-1} in stages S5 and S6, respectively.

6.2.3. Analytical procedures

VMS concentration analysis in the gas phase at the inlet and outlet of the BTFs was carried out in an Agilent 8860 gas chromatograph (Santa Clara, California, USA) equipped with a flame ionization detector (FID) and a HP-5 column (15 m × 0.25 mm × 0.25 µm). Both the detector and injector temperatures were maintained constant at 250 ºC. The oven temperature was initially set at 40ºC for 2.0 min, then increased at 30 ºC min^{-1} up to 180 ºC, maintained for 1 min and increased again at 30 ºC min^{-1} to 200 ºC. Helium was used as the carrier gas at a flow rate of 3.5 mL min^{-1}.

CO_2 and O_2 gas concentrations were daily determined in a Bruker 430 gas chromatograph (Palo Alto, USA) coupled with a thermal conductivity detector and equipped with a CP-Molsieve 5A (15 m × 0.53 mm × 15 µm) and a P-PoraBOND Q (25 m × 0.53 mm × 10 µm) columns. Oven, detector and injector temperatures were maintained constant at 45, 200 and 150 °C for 5 min, respectively. Helium was used as the carrier gas at a flow of 13.7 mL min^{-1}.

The total organic carbon (TOC), total inorganic carbon (IC), total nitrogen (TN), silicone (Si), nitrite and nitrate concentrations in the cultivation broth were periodically analyzed. Silicon concentration was analyzed by means of an inductively coupled plasma optical atomic emission spectrometer (ICP-OES Radial Simultaneous Varian 725-ES, Agilent). TOC, IC and TN concentrations were measured using a TOC-VCSH analyzer coupled with a TNM-1 chemiluminescence module (Shimadzu, Japan). Finally, nitrite and nitrate were determined in a HPLC-IC using a Waters 515 HPLC pump coupled with a conductivity detector (Waters 432) and equipped with an IC-PAK Anion HC column (4.6 × 150 mm) and an IC-Pak Anion Guard-Pak (Waters).

6.2.4. Bacterial community analysis

Samples were taken at the end of operation of the anoxic and aerobic BTFs (BTF-AN and BTF-AE). For this, the biofilm from the Kaldnes K1 Micro rings was resuspended in 40 ml of TE buffer pH 7.4. For RNA preservation, the 40 ml of culture were centrifuged for 10 min at 10,000 *g* at 4 °C and the cell pellet was washed once with 10 ml of TE buffer pH 7.4. After a second centrifugation, the pellet was snap-frozen and stored at -80 °C. RNA extraction in triplicate (biological replicates) and Illumina Miseq amplicon sequencing were carried out in the Foundation for the Promotion of Health and Biomedical Research of the Valencia Region (FISABIO, Spain). RNA extraction was conducted using the RNA PowerSoil® Total RNA Isolation Kit. The RNA extracts were subjected to DNase treatment using the DNase I Kit for Purified RNA in Solution (Mobio Laboratories Inc.) for removal of residual DNA. RNA and DNA concentration was determined using the Qubit® RNA Assay Kit in Qubit® 2.0 Fluorometer (Life Technologies, Carlsbad, CA). RNA integrity was assessed using the RNA Nano 6000 Assay Kit of the Agilent Bioanalyzer 2100 system (Agilent Technologies, CA, USA). The RNA was subsequently converted to cDNA using the qScriber™ cDNA Synthesis Kit (Mobio Laboratories Inc.). Sequencing was performed by Illumina Miseq platform targeting the 16S V3 and V4 regions (464bp, *Escherichia coli* based coordinates) with the bacterial primers S-D-Bact-0341-b-S-17 and S-D-Bact-0785-a- A-21 according to (Pascual et al., 2021). Archaea communities were not targeted due to the lack of PCR amplification using Archaea specific primers (Pausan et al., 2019). The 16S rRNA gene sequences were processed and quality filtered using Mothur v1.45.3 following the Mother

SOP (https://www.mothur.org/wiki/MiSeq_SOP) (Kozich et al., 2013). Sequences were then classified and annotated into Operational Taxonomic Units (OTUs) using the Ribosomal Database Project (trainset18) with 100 bootstrap iterations and 80% confidence cutoff (Cole et al., 2014). For the accuracy and convenience of taxonomic assignment to species of the most relevant microorganisms, the most abundant sequences were blasted using NCBI. The 16S rRNA gene sequences of the species obtained and their closest relatives were collected from GenBank and updated or supplemented them to the currently RDP 16S rRNA gene database (version 18) used by Mothur (provided as Supplemental Material S6). The nucleotide sequence dataset obtained in this study has been deposited at DDBJ/ENA/GenBank as bioproject: SUB12222863. After sequence cleaning and taxonomic classification, diversity studies were carried out (Willis, 2019). The rarefaction with 599 randomizations showed that the smallest representative library was obtained with 41443 reads. Alpha diversity was calculated with the Inverse Simpson Index resulting from the three biological replicates in each condition using Mothur v1.45.3 (Phandanouvong-Lozano et al., 2018). Beta diversity among samples was compared by using the Jaccard Index and AMOVA at $p<0.05$ of the triplicates (Schloss, 2008). The results obtained of the prokaryotic community structure were plotted using R version 4.1.2 (Team, 2016) with the package *pheatmap* (Kolde, 2019).

6.3. Results and Discussion

6.3.1 Abiotic test

During stages I, II and III of the abiotic test, no decrease in outlet VMS concentration was observed in the empty PVC column (I), after the addition of the packing material (II) and the startup of the MSM recycling (III), remaining at similar values compared to the inlet concentration (Figure S1).

Similarly, no significant differences were observed between L2 inlet and outlet concentrations when the silicone oil was added to the recycling liquid during stage IV. However, an instantaneous decrease in the outlet concentration was recorded for the rest of the VMS associated with their absorption in the silicone oil. The outlet concentration tended to increase as the silicone oil saturated with time. No CO_2 production was recorded throughout the entire abiotic test.

6.3.2 Optimization of internal liquid and gas recirculation

Influence of the trickling liquid velocity

Both systems were inoculated after the abiotic test. During S1, the anoxic TP-BTF immediately stabilized at an average total VMS removal efficiency (RE) of 46.7 ± 5.6% by day 9, corresponding to an EC of 83.4 mg m^{-3} h^{-1} (Figure 6.2A, Table S1). A higher performance was recorded for D5 (Figure 6.3) (66.2 ± 4.6 %) compared to the rest of the VMS (37.5 ± 4.5, 37.6 ± 7.7 % and 47.7 ± 7.7 % for L2, L3 and D4, respectively). In the aerobic TP-BTF, a total VMS removal of 38.8 ± 3.7 % was achieved (Figure 6.2B, Table S1), corresponding to an EC of 92.0 mg m^{-3} h^{-1} associated with the slightly higher inlet VMS concentration (237 mg m^{-3} compared to 178 mg m^{-3} in the anoxic BTF). Similar to the anoxic system, the highest performance was recorded for D5 (72.8 ± 2.9%) compared with the rest of VMS (17.0 ± 1.7%, 17.7 ± 1.8% and 45.0 ± 7.9% for L2, L3 and D4, respectively) due to its lower vapor pressure and higher affinity for the organic phase (Figure 6.4). This superior performance for D5 compared to D4 and the linear VMS has been consistently reported (Boada et al., 2020; Pascual et al., 2021).

Previous research has demonstrated that the mass transfer coefficient and the growth of the biomass in a TP-BTF increased at increasing TLVs (Bu et al., 2021). In this sense, Caicedo et al. (2018) observed a progressive improvement in the RE and EC of toluene and ethylbenzene by subsequently increasing the TLV from 2 to 4, 15 and 20 m h^{-1} (Caicedo et al., 2018). In our system, the increase in the TLV from 2 to 10 m h^{-1} during S2 resulted in an enhancement in the VMS abatement performance of both anoxic and aerobic BTFs, reaching average RE values of 54.6 ± 3.7 and 46.5 ± 3.2%, respectively. It is worth noting that this enhancement was more remarkable for the linear VMS, with an increase in their removal by up to 1.3 and 2 times in the anoxic and aerobic TP-BTFs, respectively, compared with S1. On the contrary, the RE of the cyclic VMS remained at similar values in both systems (Table S1).

Thus, the TLV was further increased to 20 m h^{-1} during S3. However, this rise did not trigger a positive effect and lower total VMS REs of 38.0 ± 3.3 and 31.4 ± 4.6% were recorded for both anoxic and aerobic BTFs, corresponding to ECs of 85.2 ± 12.0 and 80.8 ± 6.0, mg m^{-3} h^{-1}, respectively. This decrease was especially significant for L2, L3 and D4. In particular, RE values of 19.1 ± 4.9, 33.8 ± 4.1 and 37.6 ± 3.1% were obtained in the anoxic TP-BTF, with even lower removal performances in the aerobic BTFs of 13.6 ± 1.8, 13.5 ± 2.1 and 30.7 ± 4.8% for L2, L3, and D4, respectively. Nevertheless, no significant variations were observed for D5 compared to the previous stages, remaining at RE values of 66.0 ± 4.2 and 68.2 ± 8.1% in the anoxic and aerobic TP-BTFs, respectively. According to literature, the negative effect of increasing the TLV can be associated to biofilm detachment, and particularly in BTFs packed with granular activated carbon and plastic rings (Bu et al., 2021).

The TLV was decreased back to 10 m h^{-1} during S4 in order to restore previous performance of both systems. However, none of the 2P-BTFs recovered the preceding REs, remaining at similar values compared to stage S3 in the anoxic BTF, and even slightly lower values in the aerobic BTF (Table S1).

Overall, a lower abatement performance than that obtained by the authors in previous studies under aerobic conditions was achieved under the optimum conditions tested (i.e. those of Stage 2). In these studies, total VMS removals up to 70% were observed working at the same EBRT and silicone oil fraction. Similarly, L2, L3 and cyclic VMS removals were 60, 70, and 90%, respectively. However, it should be noted that the inlet VMS concentration was 2× and 3× higher compared to the present study, which could boost mass transfer associated with an increased concentration gradient (Pascual et al., 2021, 2020). However, under anoxic conditions, the BTF performed similarly when working at the same EBRT and inlet VMS concentration with a silicone oil fraction of 45% and a TLV of 2 m h^{-1} (Pascual et al., 2022a).

Other authors have tested alternative strategies to improve the removal of these pollutants. For instance, the addition of an adsorbent material (20% of activated carbon) to the packed bed resulted in an increase in the VMS mass transfer in an anoxic BTF and allowed the reduction of the EBRT to 12 min. However, lower REs of 16% and 45 % were recorded for D4 and D5, respectively (Santos-Clotas et al., 2019). Under aerobic conditions, Li et al. achieved a comparable removal of 74 % for D4 at an EBRT of 13.2 min in a BTF inoculated with *Pseudomonas aeruginosa S240*. This good performance was associated to the presence of biosurfactants in the cultivation broth, as the gas/liquid partitioning coefficient is 7 times lower in the aqueous solution containing biosurfactants. However, the performance of this system for linear VMS was not studied (Li et al., 2014).

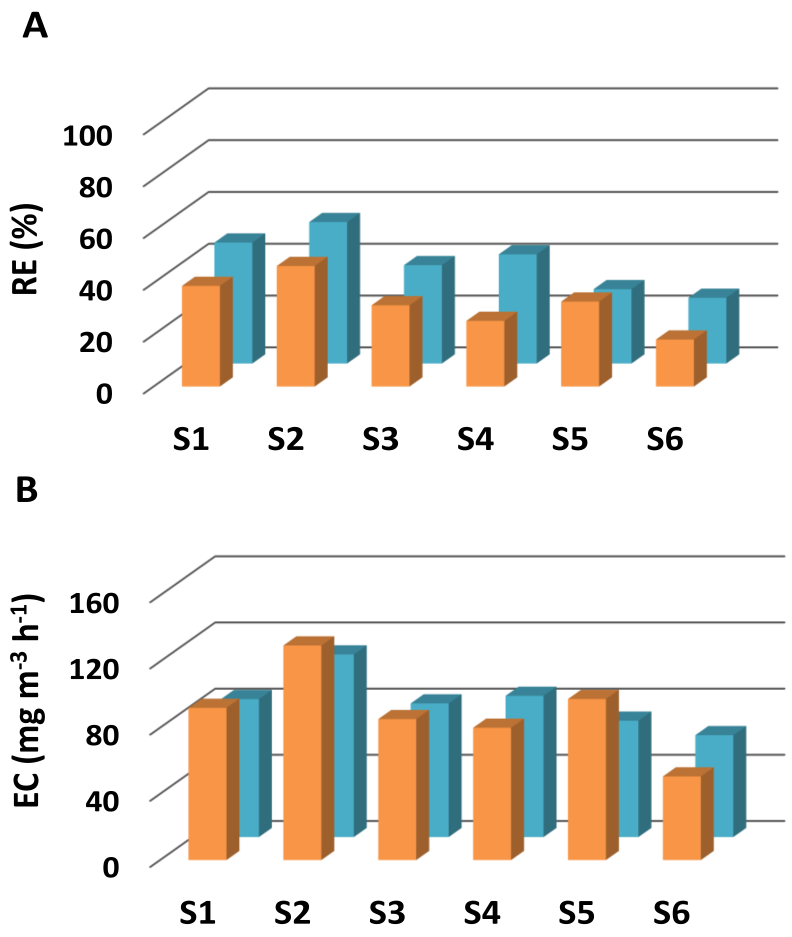


Figure 6.2. Comparison of the average VMS inlet concentration (A), removal efficiencies (B) and elimination capacities (C) in the aerobic (orange bars) and anoxic (blue bars) TP-BTFs in the different experimental stages: TLV of 2 m h^{-1} (S1), 10 m h^{-1} (S2, S4, S5 and S6), 20 m h^{-1} (S3) and internal gas recirculation of 1 L min^{-1} (S5) and 3 L min^{-1} (S6).

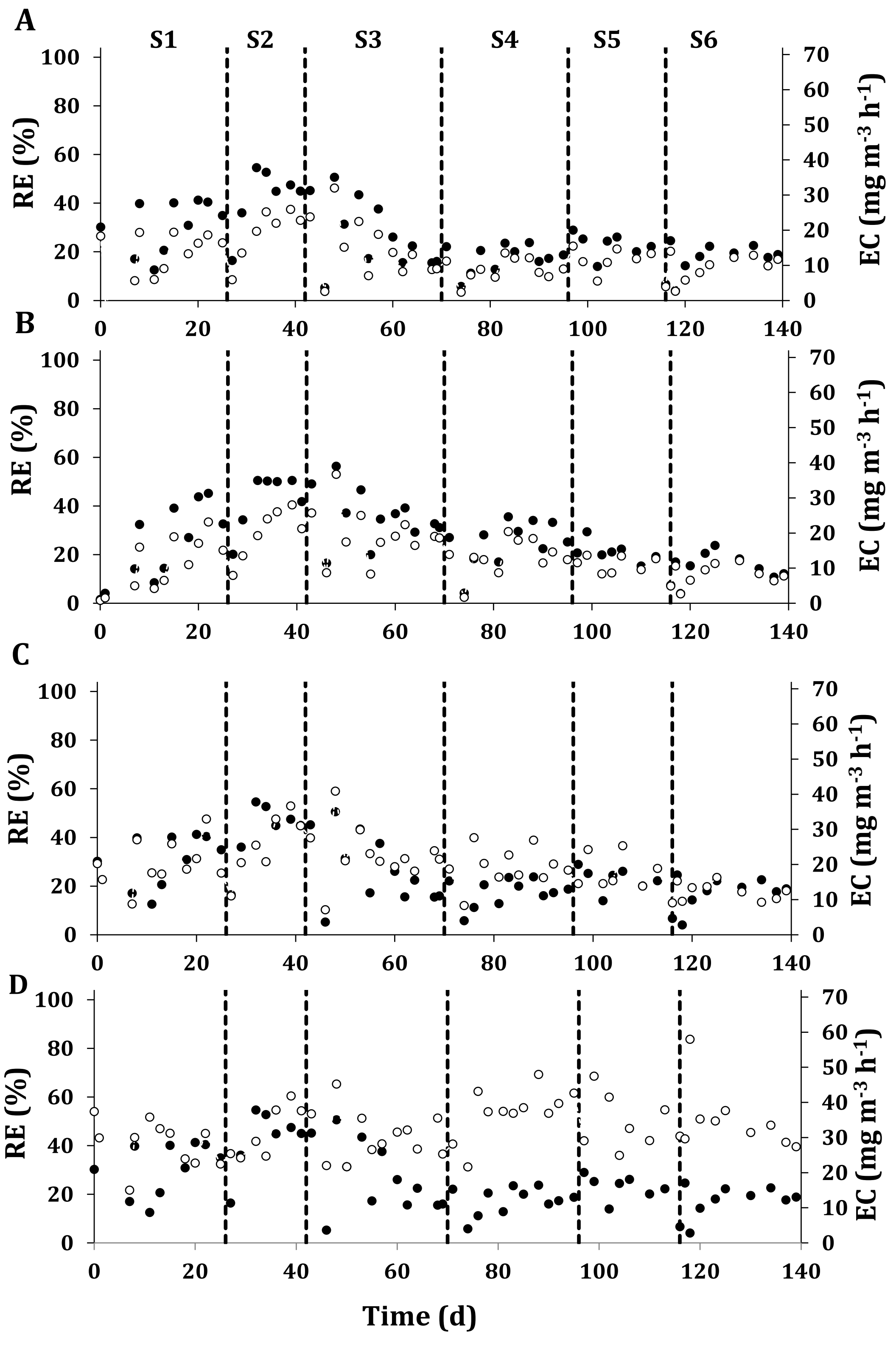


Figure 6.3. Time course of L2 (A), L3 (B), D4 (C) and D5 (D) removal efficiency (●) and elimination capacity (○) in the anoxic TP-BTF during the different experimental stages: TLV of 2 m h^{-1} (S1), 10 m h^{-1} (S2, S4, S5 and S6), 20 m h^{-1} (S3) and internal gas recirculation of 1 L min^{-1} (S5) and 3 L min^{-1} (S6).

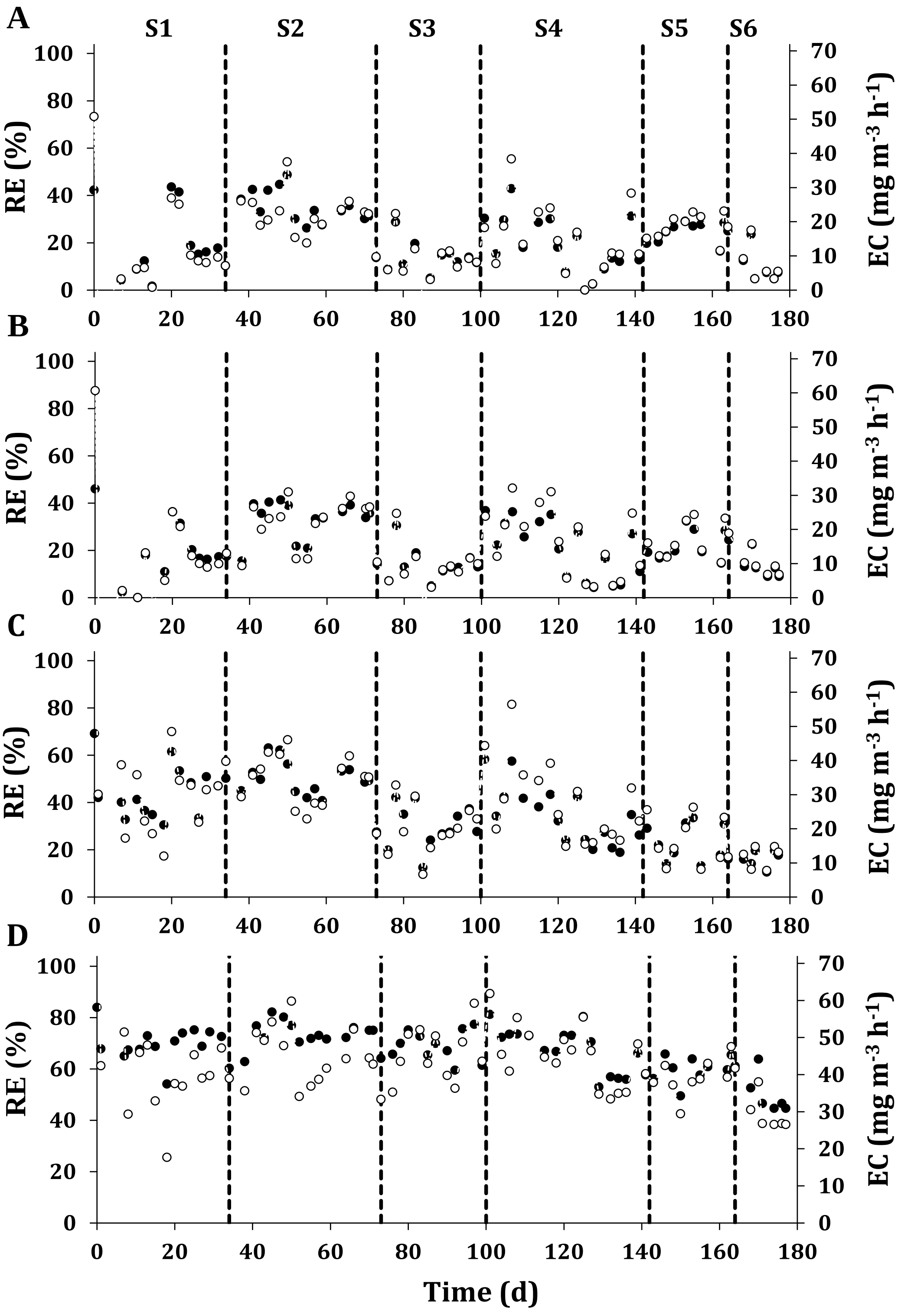


Figure 6.4. Time course of L2 (A), L3 (B), D4 (C) and D5 (D) removal efficiency (●) and elimination capacity (○) in the aerobic TP-BTF during the different experimental stages: TLV of 2 m h^{-1} (S1), 10 m h^{-1} (S2, S4, S5 and S6), 20 m h^{-1} (S3) and internal gas recirculation of 1 L min^{-1} (S5) and 3 L min^{-1} (S6).

Influence of the internal gas recirculation

During S5, an internal gas recirculation of 1 L min^{-1} was implemented in both the anoxic and aerobic BTFs in order to increase the mass transfer of the hydrophobic VMS. The total VMS RE in the anoxic TP-BTF initially increased up to 70 %, subsequently decreasing to average steady state values of 28.7 ± 7.8% (Figure 6.2). No improvement in the performance of the system was observed for L2 compared to previous stages. However, the RE decreased to 16.1 ± 6.4, 24.5 ± 10.8 and 59.1 ± 6.9% for L3, D4 and D5, respectively (compared to those of S4) (Table S1). On the contrary, a notable increase in the RE was observed in the aerobic TP-BTF, stabilizing at average values of 32.8 ± 4.9 %. An increase in the performance of the system was observed for L2, L3 and D5, reaching REs of 25.0 ± 5.7, 22.9 ± 7.0 and 60.9 ± 3.3%, respectively. On the contrary, no improvement was observed for D4 (Table S1).

In order to further studying the effect of the internal gas recirculation, this flow was increased to 3 L min^{-1} during S6. No significant effect was observed in the anoxic BTF, reaching slightly lower RE values of 25.4 ± 2.2%. This detrimental effect was more significant for D4, whose removal was reduced by 30%. On the contrary, the performance of the aerobic TP-BTF was greatly reduced, with the total VMS RE decreasing by a factor of 1.8.

To the best of the authors' knowledge, internal gas recirculation has not previously been implemented in a BTF intended for siloxanes removal. This configuration has been studied in a BTF for methane removal (Estrada et al., 2014), concluding that the internal gas recirculation improves the performance of the systems by 2.5 times due to an increase in the pollutants mass transfer, as it decouples the gas-liquid turbulence inside the reactor from the actual gas residence time. However, excessive high recirculation flow rates could damage the biofilm in the BTF due to the shear stress resulting from the turbulence, as observed in the present study, or create preferential pathways inside the packed bed. In our particular study, the biofilm, likely affected by the high TLV implemented in the previous stages (20 m h^{-1}), did not withstand the turbulence generated in the system. Similarly, Dupnock and Deshusses (2019) observed a decrease in the hydrogen removal by 15% when the internal gas recirculation was implemented in a BTF (Dupnock and Deshusses, 2019). The authors concluded that the implementation of the internal gas recirculation in plug flow systems, such as BTFs, decreased the concentration at the inlet of the bioreactor, where the mass transfer is faster due the higher concentration gradient. Hence, this strategy might result more efficient in bioreactors with suspended biomass, such as bubble column or airlift bioreactors, where the implementation of gas recirculation entails the increase of the gas holdup and gas-liquid interfacial area.

6.3.3. Influence of operating conditions on CO_2 production and characterization of the recycling liquid solution.

The CO_2 production in the anoxic TP-BTF related to the microbial activity and the biodegradation of VMS stabilized at average values of 373 ± 41 mg m^{-3} h^{-1} and remained constant throughout the stages S1, S2, S3 and S4 (where the influence of the trickling liquid velocity was tested) (Figure S2.A). At the beginning of stage S5, a gradual increase in the CO_2 production to 614 mg m^{-3} h^{-1} was recorded in the anoxic TP-BTF, remaining at 533.2 ± 77.4 mg m^{-3} h^{-1} until the end of the experiment. The inorganic carbon concentration in the recirculating cultivation broth (Figure S3.A), associated with the dissolved CO_2, gradually increased to values of 38.6 mg L^{-1} by day 62 and stabilized at average values of 34.4 ± 0.7 mg L^{-1} during stage S4. Then, the IC concentration continuously increased to reach a maximum concentration of 47.6 mg L^{-1} by day 125, slightly decreasing by the end of the experiment.

In the aerobic BTF, the CO_2 production remained constant at 1530 ± 179 mg m^{-3} h^{-1} until day 48 (Figure S2.B), when a sharp increase to 12215 mg m^{-3} h^{-1} was recorded in the system. This value gradually decreased to 6525 mg m^{-3} h^{-1} by day 69 and increased again at the beginning of S3. The IC concentration, similar to CO_2 production, remained at average values of 1.6 ± 0.3 3 mg L^{-1} until day 53, when it increased to a maximum value of 29.5 at the beginning of S3. Then, the IC concentration gradually decreased to 4.8 mg L^{-1} by day 116, fluctuating by the end of the experiment between 6.3 and 19.1 mg L^{-1} (Figure S3.B). These variations were observed throughout the experiment, which were associated with occasional cell debris from biofilm detachment and the subsequent degradation of the organic carbon released to the trickling solution.

The higher CO_2 production values achieved in the aerobic TP-BTF compared to the anoxic system were attributed to both the higher TOC concentration and the presence of O_2 in the trickling solution, which could have triggered the aerobic degradation of residual organic matter (Figure S3). The TOC concentration in the anoxic TP-BTF progressively increased to 70.4 mg L^{-1} in stage S3 (day 48), and then decreased to 37.0 mg L^{-1} (day 69). During S4 and S5, the TOC concentration remained at an average value of 51.4 ± 3.0 mg L^{-1}, gradually increasing in S6 to average values of 69.4 ± 2.6. However, the TOC concentration in the aerobic TP-BTF sharply increased at the beginning of the experiment to 155.9 mg L^{-1} by day 11, progressively decreasing to values of 72.4 mg L^{-1} by day 46. TOC accumulated again in the system during S2, achieving maximum values of 242.5 mg L^{-1} by day 60. The concentration remained roughly constant until day 88, stablishing afterwards at 156.8 ± 15.9 mg L^{-1}.

Similar to the TOC concentration, the Si concentration (Figure S4.A) in the anoxic TP-BTF gradually increased to 13.5 mg L^{-1} by day 48, then decreasing to 5.9 mg L^{-1} at the end of stage S3. The same trend was observed during S4, increasing to 10.2 mg L^{-l} likely due to the removal of siloxanes, and decreasing afterwards to 3.4 mg L^{-1} by day 97. Finally, the Si concentration stabilized at 5.3 ± 0.5 mg L^{-1}. In the aerobic BTF, the Si concentration progressively increased to 7.2 mg L^{-1} by day 88, remaining at an average value of 6.8 ± 0.7 mg L^{-1} during stages S3 and S4 (Figure S4.A). Afterwards, the Si concentration slightly decreased to 5.3 mg L^{-1} at the end of the experiment (Figure S4.B). According to the mass flow rate of siloxanes removed in both anoxic and aerobic TP-BTF, and the replacement of MSM, an accumulation of Si up to 208 and 285 mg L^{-1}, respectively, was expected in the aqueous phase (assuming that all the Si removed ended up in the aqueous phase). Despite the Si content in the organic fraction was not analyzed, the stabilization of Si concentration in the aqueous phase indicated that part of the Si removed was assimilated by the microbial community.

The TN, nitrate, and nitrite concentrations (Figure S5) in the anoxic TP-BTF remained at 323.4 ± 15.4 mg L^{-1}, 255.8 ± 16.0 mg $N\text{-}NO_3^-$ L^{-1} and 15.2 ± 5.7 mg $N\text{-}NO_2^-$ L^{-1}, respectively. The trace levels of nitrite observed were associated with the incomplete denitrification under anoxic conditions. In the aerobic BTF, TN and nitrate concentrations between 300 and 400 mg N L^{-1} were recorded throughout the entire experiment, while no nitrite was detected regardless of the stage.

6.3.4. Active bacterial community and diversity

The analysis of the active bacterial community resulting from the RNA analysis displayed a total of 388761 sequences that belonged to 2784 OTUs affiliated with bacterial genera. By the end of the operation, similar number of genera were found in both BTFs (244 and

218 total in the anoxic and aerobic BTFs, respectively). However, the bacterial communities shared less than 20 % of the identified genera, which was related to the different metabolic conditions (aerobic and anaerobic conditions). In accordance to these results, bacterial alpha and beta diversity was highly dissimilar (AMOVA, $p < 0.05$) between the two BTFs operated (Figure S6).

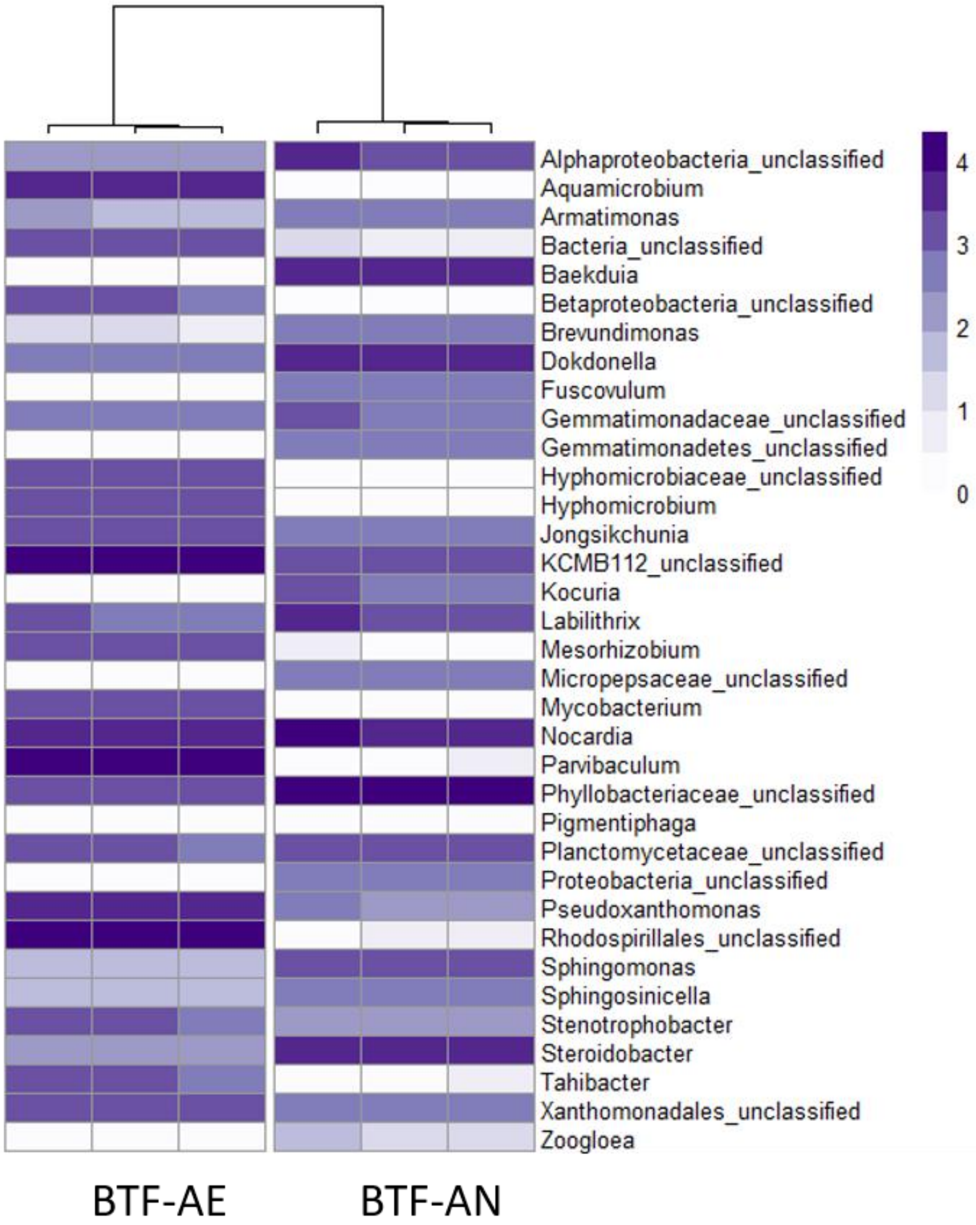


Figure 6.5. Heat map of the most representative bacterial groups (99 % of the total genera) in the aerobic and anoxic BTFs at the end of the experiment (in triplicate). Data is presented as the log transformation of the relative abundance per sample. The dendrogram on top represents hierarchical clustering of the sample replicates.

The analysis of the bacterial taxonomic classification showed that the different conditions in the BTFs resulted in a highly dissimilar specialized active consortium (Figure 6.5). The most abundant active bacteria in the anoxic TP-BTF were uncultured members of the family *Phyllobacteriacea* (21.0 ± 0.9%), followed by the genera *Nocardia* (14.8 ± 0.4) and *Baekduia* (12.7 ± 0.4%), respectively. Other dominant bacteria belonged to the genera *Steroidobacter* (9.3 ± 0.2), *Dokdonella* (7.5 ± 0.3%), *Sphingomonas* (3.7 ± 0.2%), and uncultured Proteobacteria of the clade *Acidithiobacillaceae KCM-B-112* (3.0 ± 0.1%).

In the aerobic BTF, the most representative active bacteria were unclassified members of the order Rhodospirillales (27.2 ± 0.1%), uncultured Proteobacteria of the clade *Acidithiobacillacea* KCM-B-112 (22.6 ± 0.1%) and the genera *Parvibaculum* (11.8 ± 0.2%), followed by the genus *Nocardia* (7.1 ± 0.3%), *Aquamicrobium* (5.4 ± 0.5%) and *Pseudoxanthomonas* (5.2 ± 0.4%).

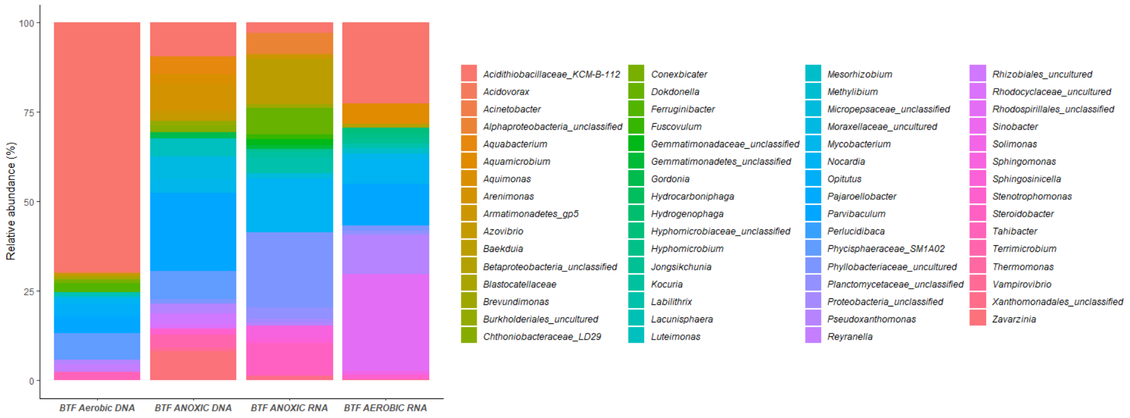


Figure 6.6. Stacked bar graph of the total bacterial genera found in the aerobic and anaerobic BTFs when there was DNA extraction (Pascual et al. 2022) or RNA extraction (present study).

Regarding the anoxic TP-BTF, the bacterial groups found in the RNA study, showed again that KCM-B112 was an active group, although the most dominant bacterial groups were members from the family *Phyllobacteriacea*, followed by the genera *Nocardia* and *Baekduia*. These genera did not represent high abundances in the BTF operated anaerobically for 126 days. This was associated with: i) the analysis of RNA performed in this study, that shows the active bacteria population; ii) the high turbulence generated in the system that may have weakened the biofilm favoring those bacteria that are more resistant to shear stress.

In a previous reactor operated under aerobic (124 days) conditions the main bacteria found according to their 16S rRNA gene belonged to the clade *Acidithiobacillaceae_KCMB-112* (65.3 ± 0.2 %), and the genera *Opitutus* (7.6 ± 0.1 %) and *Parvibaculum* (5.8 ± 0.1 %) (Pascual et al., 2021, 2020). This study confirmed that the clade *Acidithiobacillaceae_KCMB-112* and the genera *Parvibaculum* were among the most active bacterial members under aerobic conditions and they most likely have an important role in the degradation of siloxanes. However, the dominant order Rhodospirillales, along with other active representative genera (such as *Nocardia*, *Aquamicrobium* and *Pseudoxanthomonas*) had a relative low abundance according to the DNA analysis, while they appeared as important active bacterial groups after specialization in the aerobic BTF operated according to the RNA analysis.

Interestingly, some bacteria (members of *Acidithiobacillaceae* and the genus *Nocardia*) were rather active under anaerobic and aerobic conditions. Several *Acidithiobacillaceae* members are facultative anaerobes able to grow as chemolithoautotrophs in complex environments (Osorio et al., 2019). In previous works, they were recurrently present in reactors treating siloxanes, and it may be possible that they can feed on siloxanes using oxygen and nitrate as electron acceptor. In the case of *Nocardia*, this genus has been classified as a silicon utilizing bacteria (Das, P. ; Das, 2010; Das et al., 1992). However, all the members of *Nocardia* are strictly aerobic. Thus, their high relative abundance under anaerobic conditions is difficult to justify. Nevertheless, bacteria belonging to the family *Phyllobacteriacea*, such as the genus *Nitratireductor* (Baek et al., 2020), or the genera *Steroidobacter* (Fahrbach et al., 2008; Sharma et al., 2018), *Sphingomonas* (Li et al., 2015) have been classified as anaerobic bacteria capable to degrade complex organic compounds. Therefore, they could be involved in the oxidation of siloxanes in anoxic conditions using the nitrate present in the culture broth. Moreover, *Aquamicrobium* has been pointed as able to degrade organic pollutants by using both nitrate and oxygen as electron acceptor. Overall, this study revealed the active bacterial population according to the transcriptome when siloxanes were the sole carbon source present.

6.4. Conclusions

The present research brought about important advances in the biodegradation of siloxanes by means of the study of the bacterial community and the implementation of enhanced mass transfer strategies. On the basis of the improvement that TP-BTF entails in the mass transfer of siloxanes, the increase in the TLV from 2 to 10 m h^{-1} enhanced the performance of both anoxic and aerobic TP-BTFs from 47 to 55% and from 39 to 47%, respectively. This effect was more remarkable for the linear VMS, resulting in an increase in the removal performance of 40%. Both L2 and L3 reached similar maximum REs, around 49% and 35% in the anoxic and aerobic TP-BTF, respectively (corresponding to ECs of ~ 23 and 25 mg m^{-3} h^{-1}, respectively). However, a further increase in the TLV to 20 m h^{-1} negatively affected the bacterial community, likely due to biofilm detachment, resulting in a decrease in the total RE in both TP-BTBs. An internal gas recirculation of 1 L min^{-1} did not significantly improve the total VMS removal performances compared to the maximum REs previously obtained, even triggering a system deterioration when the gas recirculation was increased to 3 L min^{-1}. This was associated to both a lower VMS inlet concentration entering the TP-BTF and an excessive turbulence promoted in the biofilm. Overall, the highest REs were recorded for D5 under both anoxic and aerobic conditions when operating the system at a TLV of 10 m h^{-1}, with values of 75 % corresponding to ECs around 45 mg m^{-3} h^{-1}. Moreover, D5 removal was scarcely affected by the modifications implemented in the system. In addition to these findings, this paper substantially contributes to increase the knowledge of the biological degradation of siloxanes, because this is the first time that the active bacterial population of reactors treating VMS has been studied. These results pointed that some bacterial groups are actively involved in the degradation of siloxanes.

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Appendix D. Supplementary Material

Assessment of the mass transfer strategy and the role of the active bacterial population on the biological degradation of siloxanes

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Figure S1

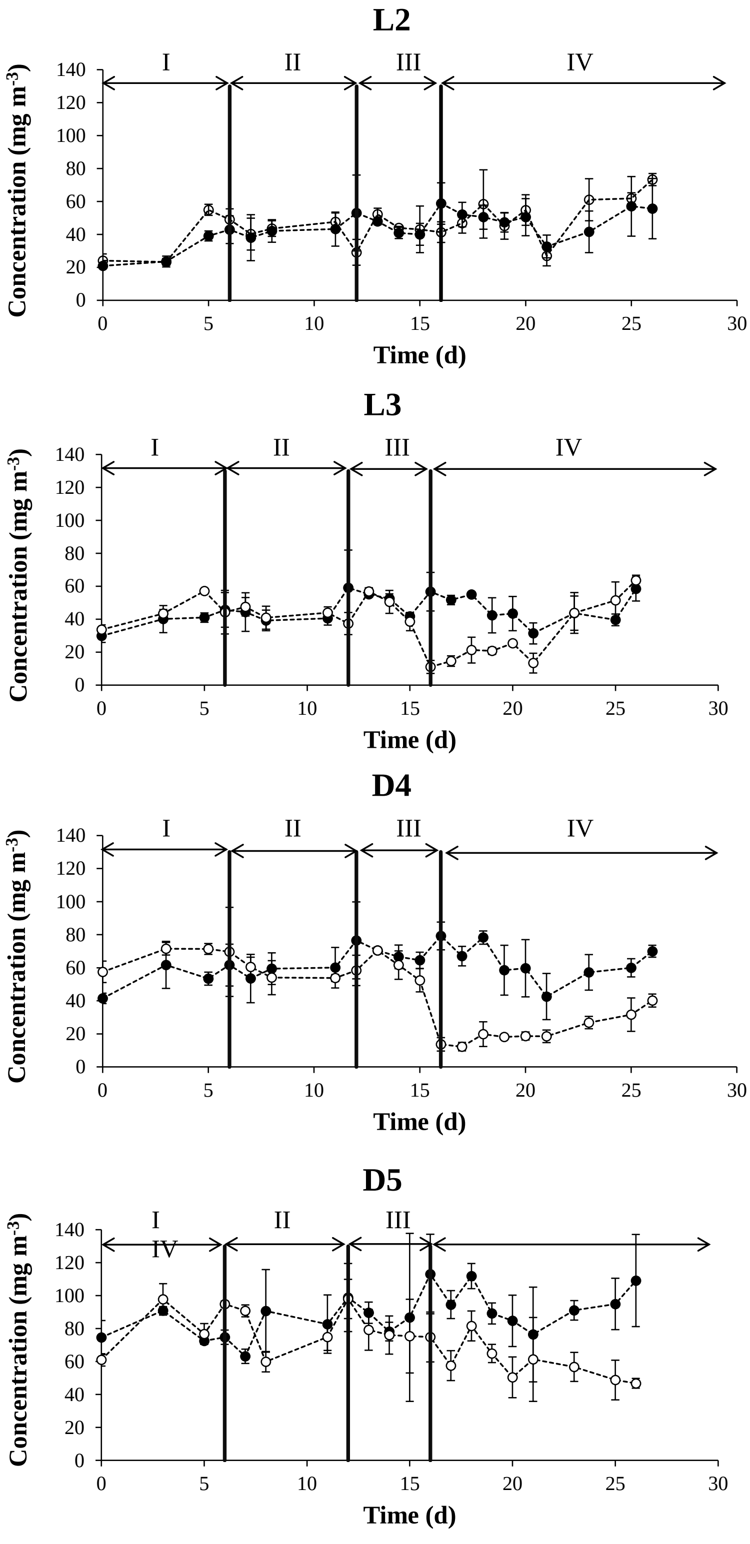

Figure S1. VMS inlet (●) and outlet (○) concentrations in the BTF during the abiotic test: empty column (I), packing material (II), mineral medium (III) and silicone oil (IV). Vertical lines represent standard deviation from replicate measurements.

Figure S2

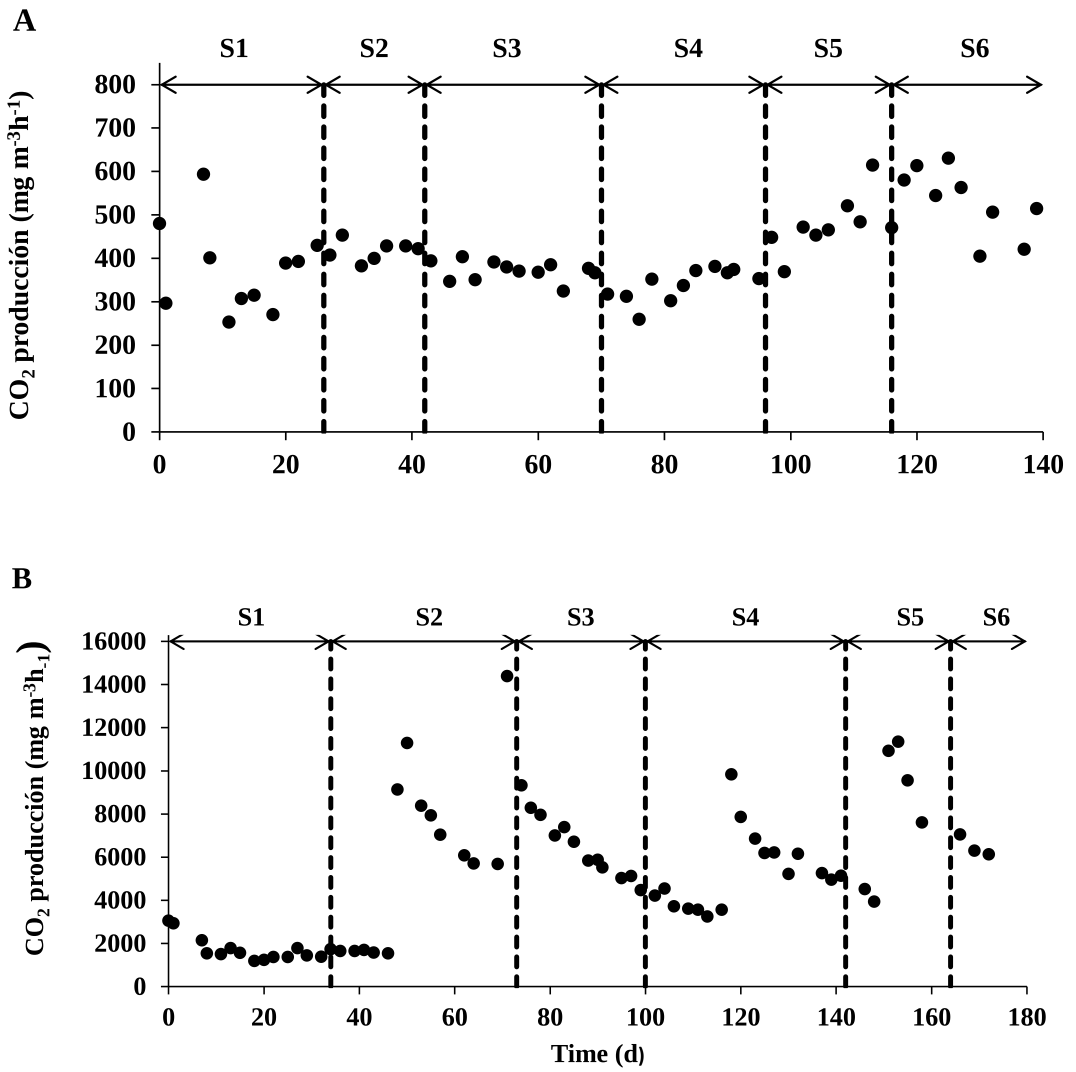

Figure S2. Time course of CO_2 production in the anoxic (A) and aerobic (B) TP-BTF during the different experimental stages: TLV of 2 m h^{-1} (S1), 10 m h^{-1} (S2, S4, S5 and S6), 20 m h^{-1} (S3) and internal gas recirculation of 1 L min^{-1} (S5) and 3 L min^{-1} (S6).

Figure S3

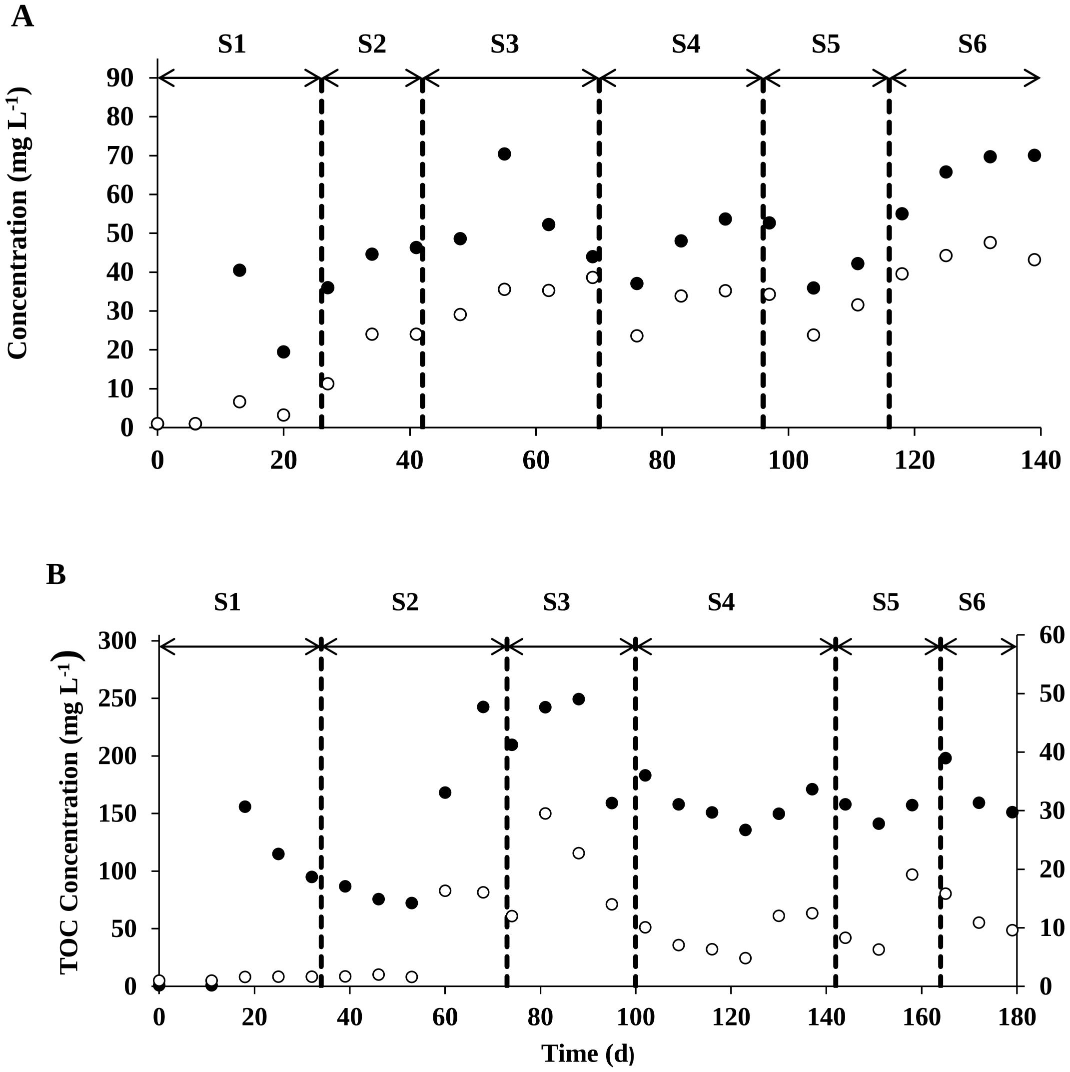

Figure S3. Time course of TOC (●) and IC (○) concentration in the aqueous phase of the anoxic (A) and aerobic (B) TP-BTF during the different experimental stages: TLV of 2 m h^{-1} (S1), 10 m h^{-1} (S2, S4, S5 and S6), 20 m h^{-1} (S3) and internal gas recirculation of 1 L min^{-1} (S5) and 3 L min^{-1} (S6).

Figure S4

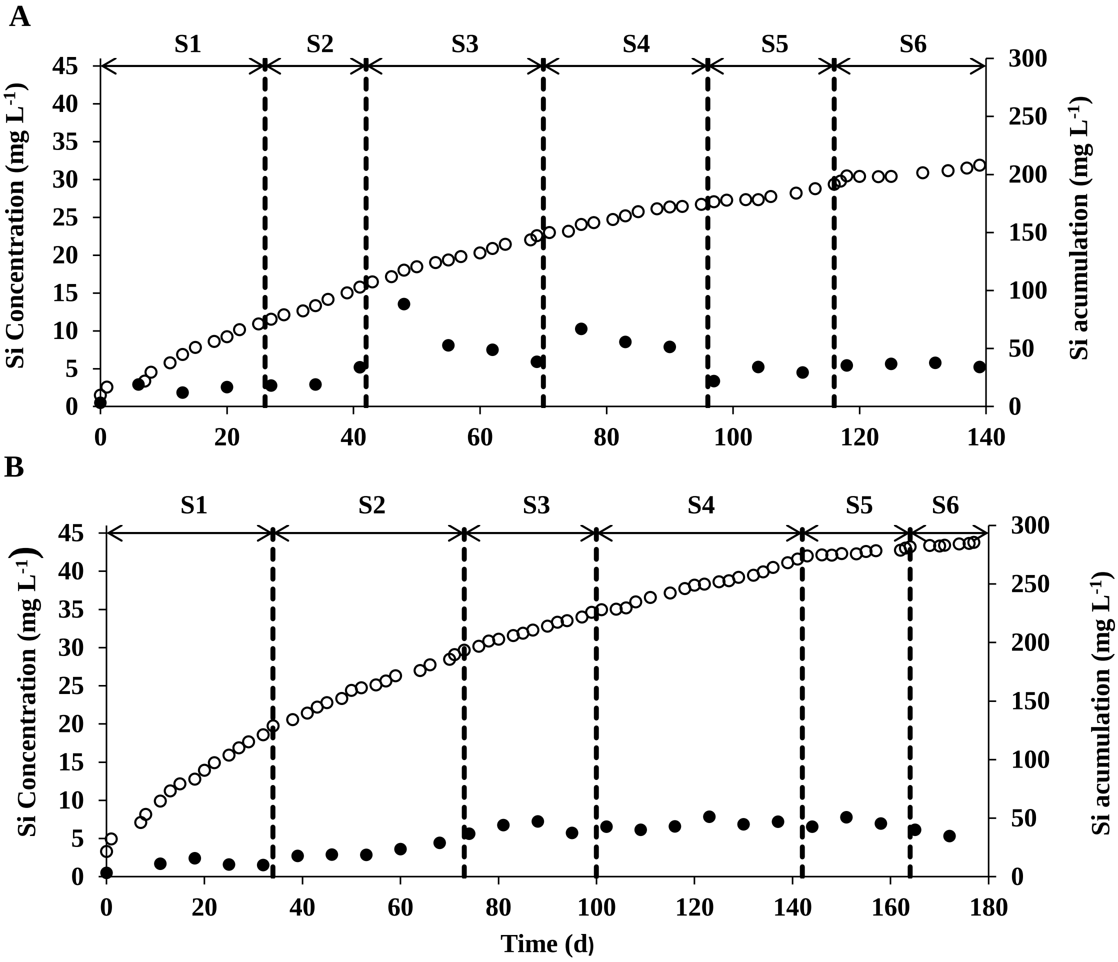

Figure S4. Time course of silicon concentration (●) and theoretical accumulation (○) (assuming that all Si removed ended up in the liquid phase) in the aqueous phase of the anoxic (A) and aerobic (B) TP-BTF during the different experimental stages: TLV of 2 m h^{-1} (S1), 10 m h^{-1} (S2, S4, S5 and S6), 20 m h^{-1} (S3) and internal gas recirculation of 1 L min^{-1} (S5) and 3 L min^{-1} (S6).

Figure S5

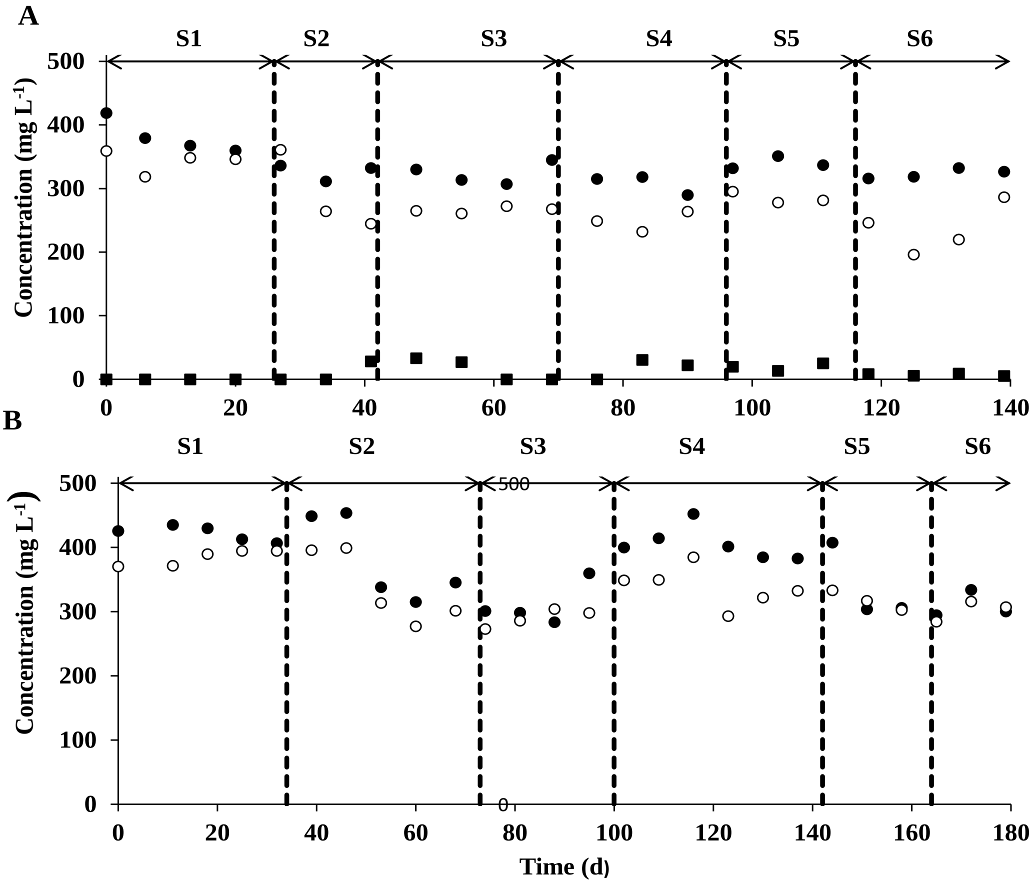

Figure S5. Time course of TN (●), N-NO$_3^-$ (○) and N-NO$_2^-$ (■) concentration in the aqueous phase of the anoxic (A) and aerobic (B) TP-BTF during the different experimental stages: TLV of 2 m h^{-1} (S1), 10 m h^{-1} (S2, S4, S5 and S6), 20 m h^{-1} (S3) and internal gas recirculation of 1 L min^{-1} (S5) and 3 L min^{-1} (S6).

Figure S6

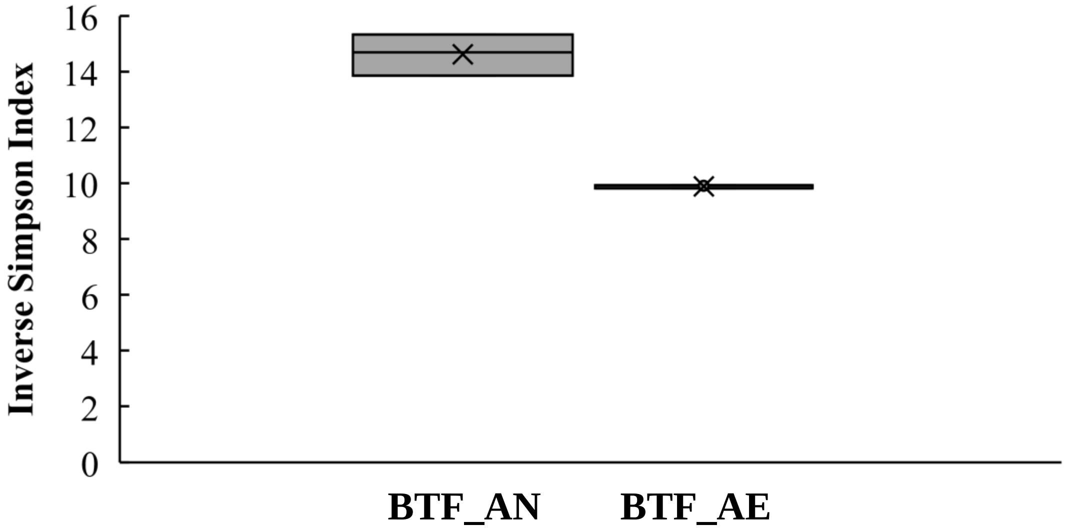

Figure S6. Bacterial alpha diversity of the samples using the Inverse Simpson Index (for the index calculation, the three triplicates have been considered). The label for the OTUs was 0.03.

Table S1

Table S1. Steady removal efficiencies (%) and elimination capacities in the anoxic and aerobic TP-BTF during the different experimental stages.

RE (%) - anoxic TP-BTF					
	L2	**L3**	**D4**	**D5**	**Total VMS**
S1	37.5 ± 4.5	37.6 ± 7.7	47.7 ± 7.7	66.2 ± 4.6	46.7 ± 5.6
S2	48.9 ± 4.5	48.6 ± 3.8	52.5 ± 7.3	67.9 ± 5.7	54.6 ± 3.7
S3	19.1 ± 4.9	33.8 ± 4.1	37.6 ± 3.1	66.0 ± 4.2	38.0 ± 3.3
S4	18.9 ± 3.4	28.8 ± 5.8	40.9 ± 6.9	74.3 ± 3.3	42.1 ± 5.1
S5	18.7 ± 8.4	16.1 ± 6.4	24.5 ± 10.8	59.1 ± 6.9	28.7 ± 7.8
S6	19.6 ± 2.1	13.9 ± 3.3	17.3 ± 1.8	52.1 ± 4.7	25.4 ± 2.2
EC (mg m^{-3} h^{-1}) - anoxic TP-BTF					
	L2	**L3**	**D4**	**D5**	**Total VMS**
S1	16.8 ± 2.4	17.0 ± 4.5	23.3 ± 6.3	26.3 ± 4.5	83.4
S2	23.1 ± 2.5	23.7 ± 3.5	29.4 ± 6.3	34.2 ± 7.1	110.4
S3	10.5 ± 2.6	19.1 ± 2.1	20.9 ± 2.2	30.2 ± 4.2	80.8
S4	8.9 ± 2.3	14.3 ± 3.1	20.4 ± 4.6	41.8 ± 4.7	85.4
S5	10.9 ± 4.8	10.2 ± 3.9	16.8 ± 7.0	32.5 ± 3.9	70.3
S6	11.6 ± 1.3	8.7 ± 2.5	11.0 ± 1.6	30.2 ± 2.8	61.6
RE (%) - aerobic TP-BTF					
	L2	**L3**	**D4**	**D5**	**Total VMS**
S1	17.0 ± 1.7	17.7 ± 1.8	45.0 ± 7.9	72.8 ± 2.9	38.8 ± 3.7
S2	31.6 ± 3.1	35.8 ± 2.2	49.2 ± 5.2	74.0 ± 2.0	46.5 ± 3.2
S3	13.6 ± 1.8	13.5 ± 2.1	30.7 ± 4.8	68.2 ± 8.1	31.4 ± 4.6
S4	13.6 ± 9.6	11.6 ± 8.9	24.7 ± 6.0	57.7 ± 4.5	25.3 ± 7.0
S5	25.0 ± 5.7	22.9 ± 7.0	23.9 ± 9.9	60.9 ± 3.3	32.8 ± 4.9
S6	6.2 ± 1.5	10.9 ± 2.1	16.9 ± 4.3	45.6 ± 1.1	18.1 ± 1.8
EC (mg m^{-3} h^{-1}) - aerobic TP-BTF					
	L2	**L3**	**D4**	**D5**	**Total VMS**
S1	9.1 ± 1.0	10.3 ± 1.4	29.7 ± 5.2	42.8 ± 4.0	92.0 ± 10.0
S2	22.8 ± 2.4	26.4 ± 2.2	35.3 ± 5.3	45.1 ± 4.2	129.7 ± 13.5
S3	9.3 ± 1.9	9.3 ± 1.6	21.0 ± 3.1	45.5 ± 9.0	85.2 ± 12.0
S4	11.5 ± 9.0	9.8 ± 8.3	20.9 ± 5.9	37.8 ± 5.6	80.0 ± 27.6
S5	19.8 ± 5.5	18.0 ± 6.9	17.4 ± 8.8	42.2 ± 4.0	97.4 ± 21.2
S6	4.4 ± 1.2	8.1 ± 1.4	12.7 ± 3.3	26.7 ± 0.2	50.5 ± 4.4

Chapter 7.

Techno-economic and environmental aspects of siloxanes removal

This chapter was adapted after its publication in *Critical Reviews in Environmental Science and Technology:*

Pascual, C., Lebrero, R., Cantera, S., 2022b. Toward a sustainable and cost-efficient biological-based platform for siloxanes removal. Crit. Rev. Environ. Sci. Technol. 1–17. https://doi.org/10.1080/10643389.2022.2044254

7.1 Background

The main technologies commercially employed for siloxanes abatement are based on physical-chemical processes. They include adsorption, absorption, catalytic processes, membrane separation, refrigeration/condensation and cryogenic methods. Among them, adsorption on activated carbon represents the most common and highly effective technology for volatile methyl siloxanes (VMS) removal, although at the expenses of high operating costs associated to the regeneration or replacement of the adsorbent. Similarly, absorption technologies are highly employed for VMS treatment, although they are also characterized by high investment and operating cost related to the use of organic solvents and the requirement of absorbent cooling to avoid solvent losses and prevent atmospheric emissions (physical absorption) or the corrosive nature of acid solutions (chemical absorption) (Ajhar et al., 2010; Arespacochaga et al., 2015; Gaj, 2017; Shen et al., 2018). The high removal performance (>90%), together with their easy operation and maintenance and the long practical experience in industrial applications tilt the balance in physical-chemical technologies' favour. However, the traditional technologies' selection criteria are currently evolving towards a more comprehensive procedure, which includes the analysis of both economic and environmental indicators. In this context, physical-chemical technologies not only show high investment and operating costs but also high environmental impacts, which goes against the principles of sustainability. Thus, biodegradation technologies, although in an embryonic stage when applied for siloxanes abatement, can certainly play a key role to decrease the negative impacts of this process. The most studied biotechnological process for VMS abatement has been biotrickling filtration (BTF). However, to date lower removal performances (around 70%) have been achieved at the expense of high gas residence times, ultimately leading to high bioreactor volumes (Li et al., 2014). Based on the outstanding performance of physical-chemical technologies versus the inferior impacts of biotechnologies, recent research evaluated a combined configuration consisting on the addition of a second polishing stage based on AC-adsorption (Zhang et al., 2021). In this way, the impacts of adsorption techniques would be reduced. However, viability of this novelty application should be further analysed.

In order to evaluate and select the best solution among the existing alternatives for the treatment of waste gases, different techno-economic and environmental analyses have been assessed as a selection criteria (Alfonsín et al., 2015; Estrada et al., 2012, 2011). Based on these studies, a simplified comparative techno-economic and environmental study of conventional and developing biological technologies for siloxanes abatement was performed in this chapter. This study included the most commonly employed physical-chemical technologies for siloxanes removal (activated carbon adsorption and chemical absorption), the best performing biotechnology tested up-to-date (BTF), and a combined configuration consisting of a BTF followed by an AC-adsorption polishing stage. The techno-economic analysis was performed using a typical biogas production of 1000 m^3 h^{-1} and the most conservative EBRT according to existing literature (300, 15, 2700 and 2715 s for chemical absorption, AC adsorption, BTF and combined BTF-AC, respectively).

7.3. Comparative discussion of the different technologies

The highest operating costs were calculated for the AC adsorption technology (7.2 €/ $(m^3/h)^{-1}$), in contrast to the BTF that showed the lowest operating costs (1.2 €/ $(m^3/h)^{-1}$) (Figure 7.1A). This expenditure results from the continuous replacement of the activated carbon after saturation of the adsorbent, which is in contrast to the long lifespan and low pressure drop of the packing material in the BTF (10 years and 500 Pa, respectively). In this sense, media replacement constitutes the main contributor to the operating costs of these technologies (66% and 44% for the AC adsorption and BTF, respectively). Chemical absorption also presented higher operating costs (3.6 €/$(m^3/h)^{-1}$) compared to the BTF associated to chemicals purchase (organic solvents and concentrated alkaline or acid solutions), with a share of 69 % to the total costs. Finally, the combined BTF-AC exhibited operating costs slightly higher (2.7 €/ $(m^3/h)^{-1}$) than those of the BTF due to the replacement of the activated carbon (41% of the total operating costs). However, these values were lower than those calculated for physical-chemical technologies. This was due to the preliminary reduction of the VMS concentration in the BTF, which increased the lifespan of the AC on the adsorption unit (Estrada et al., 2012).

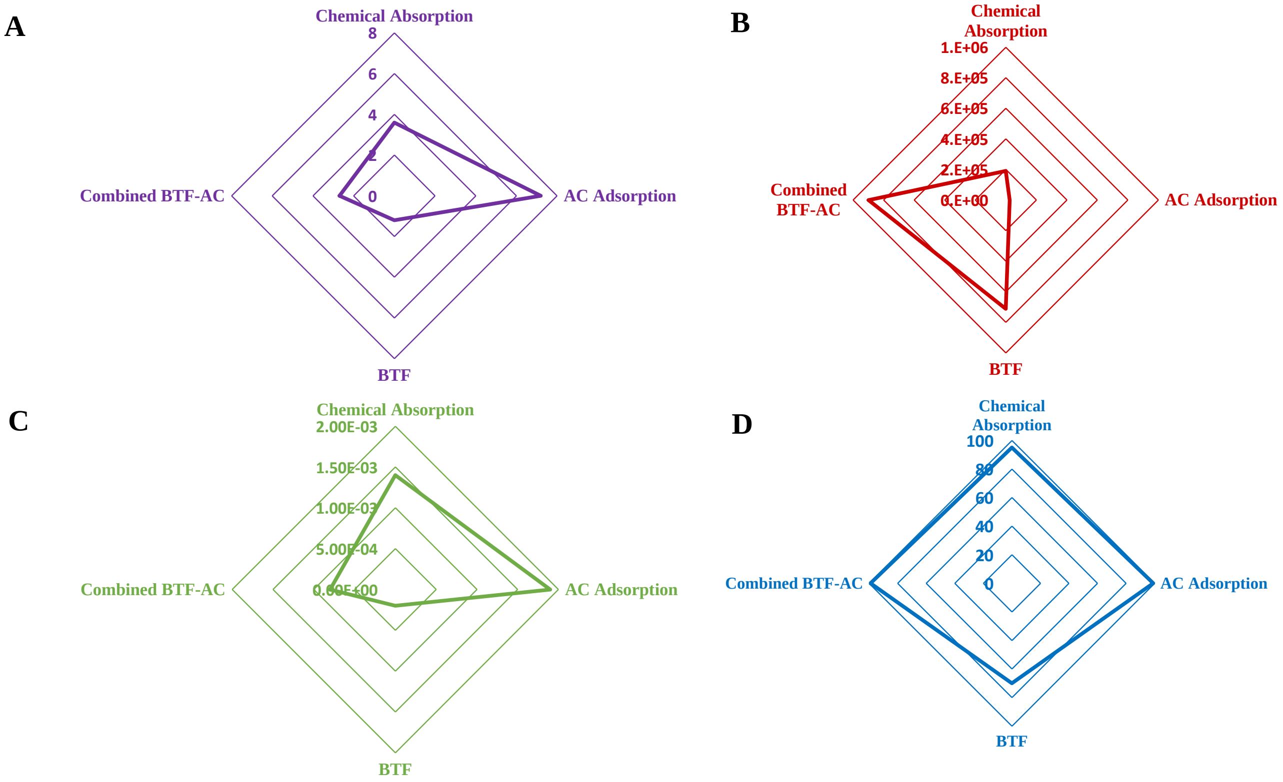

Figure 7.1. Techno-economic and environmental analysis of four different VMS removal technologies from biogas: chemical absorption, activated carbon (AC) adsorption, biotrickling filtration (BTF), and combined BTF-AC adsorption. A) Operating costs (€ $(\text{m}^3/\text{h})_{\text{treated biogas}}{}^{-1}$) per year, B) Investment costs (€), C) Environmental impact (kg CO_2 eq. m^{-3}), D) VMS removal efficiency (%).

Conversely, the highest capital investment costs were obtained for the BTF and the combined BTF-AC technology (711,698 and 898,389 €, respectively), being significantly lower for the physical-chemical processes (191,314 and 25,220 € for chemical absorption and AC adsorption, respectively) (Figure 7.1B). Nevertheless, the lower operating costs of the BTF and the combined BTF-AC alternatives might offset the initial investment expenses, thus resulting in a favourable economic balance in the long-term.

As expected, the biological technology exhibited the lowest environmental impact according to the climate change indicator (2.0×10^{-4} kg CO_2 eq. m^{-3}), followed by the combined BTF-AC (8.0×10^{-4} kg CO_2 eq. m^{-3}) (Figure 7.1C). The energy requirement was the main contributor to the climate change indicator for the BTF, while AC production and transportation increased the impact of the combined BTF-AC. On the contrary, AC adsorption (1.9×10^{-3} kg CO_2 eq. m^{-3}) and chemical absorption (1.4×10^{-3} kg CO_2 eq. m^{-3}) presented the highest CO_2 footprints due to the packing material production and transportation, chemical use and waste disposal in landfills (Alfonsín et al., 2015).

It should be noted that this analysis focuses on the exclusive removal of siloxanes. The simultaneous removal of other pollutants present in biogas, such as H_2S or volatile organic compounds, would increase the operating costs and the environmental impact of the studied technologies. For instance, competitive adsorption of different compounds will reduce the AC lifespan, thus increasing its replacement frequency. Similarly, the formation of carbonates in alkaline absorption processes (derived from the reaction of CO_2 and NaOH) increases chemical consumption and therefore, the operating cost (Shen et al., 2018). BTF will be likely the least affected technology by the simultaneous removal of other substances, since siloxanes demand higher EBRTs due to their low solubility, which is in turn a determining parameter for the investment cost.

In summary, the analysis demonstrated that biotechnologies outperform physical-chemical siloxanes abatement technologies from both an economic and an environmental point of view. However, the low VMS removal efficiencies achieved to date in BTFs (70%) limit the stand-alone implementation of this technology. In this context, the combined BTF-AC configuration could be an adequate solution for VMS removal, since the BTF unit decreases the overall environmental impact and the operating costs while the AC unit increases the removal efficiency of the global process (Figure 7.1D).

It is also worth to mention that recent advances in biotechnologies could change this current scenario. For instance, two-phase partitioning BTFs (TP-BTFs) studied in the present thesis could increase the abatement efficiency of VMS due to the high affinity of this compound for an organic phase, such as silicone oil. The industrial silicone oil has a current market price between 20 and 30 € L^{-1}, which would not significantly affect the total costs.

7.4. Conclusions

In this study, physical-chemical technologies, AC adsorption and Chemical absorption, showed the lowest capital investment costs in contrast to the BTF and the combined BTF-AC technology that showed the highest investment costs. However, the lowest operating costs and environmental impact were obtained for the BTF followed by the combined BTF-AC technology, while these indicators were significantly higher for the AC adsorption and Chemical absorption technologies. Despite the VMS removal efficiencies achieved to date in BTFs are lower than those of physical-chemical technologies, this analysis demonstrated the favourable long-term economic and environmental balance for biotechnologies, considering that recent advances could improve the current scenario.

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Chapter 8.

Siloxane abatement in a pilot scale Two Phase Biotrickling Filter in a relevant environment

8.1 Description & objectives

As previously mentioned, this thesis is part of the URBIOFIN Project (within the Horizon 2020 program of the EU under grant agreement Nº 745785). The aim of the URBIOFIN project was to demonstrate techno-economic and environmental viability of an integrated and innovative biorefinery for the transformation of the organic fraction of municipal solid waste (OFMSW) into new marketable bioproducts, chemical building blocks, biopolymers and additives (https://www.urbiofin.eu/). The biorefinery concept for OFMSW aims at maximizing the recovery of more diverse resources from MSW in addition to bioenergy, via simultaneous exploitation and remediation of waste. The urban biorefinery was composed of three interrelated main modules where each value chain was developed (Figure 8.1).

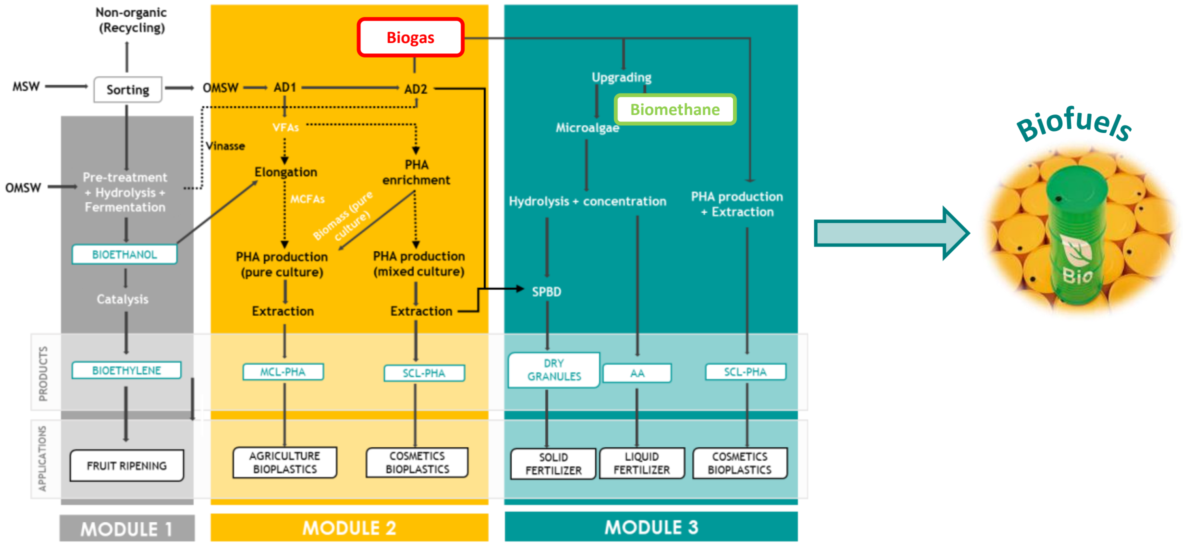

Figure 8.1. Diagram of URBIOFIN project, showing the bio-based product lines.

Module 3 was focused on the conversion of biogas to biomethane with microalgae as well as on the validation of the upgraded biomethane as a fuel for vehicles. This objective included the sustainable removal of trace compounds such as volatile methyl siloxanes (VMS), which have also consistently limited the energy use of biogas due to their detrimental effect on the equipment and piping of the process. Siloxanes contained in the biogas were removed in a final polishing step, after CO_2 and H_2S removal, to ensure a biomethane composition complying with international standards. As a result, a novel biogas upgrading biotechnology that targeted the removal of VMS, based on two-phase biotrickling filtration, was validated. The biological polishing unit for siloxane removal was moved from TRL 3 to TRL 6.

8.2 Background

The presence of VMS consistently limits the direct energy use of biogas for heat and electricity production due to their detrimental effect on the equipment and piping of the process. Current physical-chemical processes for VMS abatement (such as adsorption, absorption or condensation) entail prohibitive investment and operating costs. This drawback, along with their environmental impact, leads to considering the development of sustainable alternatives such as biological processes (Pascual et al., 2022). Despite biotrickling filtration (BTF) has been the most studied biotechnology for VMS abatement, the low aqueous solubility of VMS still limits the removal efficiencies obtained in these systems (Shen et al., 2018).

The development of a low-cost, high-mass transfer biological alternative able to efficiently remove VMS was addressed in this project. As a result, a novel final polishing stage to be implemented after the biogas upgrading process was obtained. This polishing stage consisted of a two-phase partitioning biotrickling filter (TP-BTF). In a biotrickling filter, the siloxanes-laden biomethane passes through a packed bed of synthetic inert material where microbial communities involved in VMS biodegradation are immobilized as a biofilm. A continuous recirculation of a trickling liquid solution prevents drying of the packing material, and provides nutrients for microbial growth (Urbaniec et al., 2020).

The TP-BTF is based on the mass transfer improvement of siloxanes by adding an organic water-immiscible phase with a high affinity for the gas pollutant: silicone oil. The hypothesis is that microorganisms uptake the hydrophobic gas contaminant from both the non-aqueous/aqueous interphase and from the aqueous phase, and biologically oxidize them using nitrate as electron acceptor (Lebrero et al., 2019).

8.3 Materials and Methods

The pilot-scale TP-BTF (Figures 8.2 and 8.3) consisted of a PVC column of 104 L of packed bed working volume and 52 L of holding tank used as mineral salt medium (MSM) and silicone oil reservoir. The system was installed in the Waste Technological Innovation Center "Alfonso Maíllo" (CIAM, URBASER).

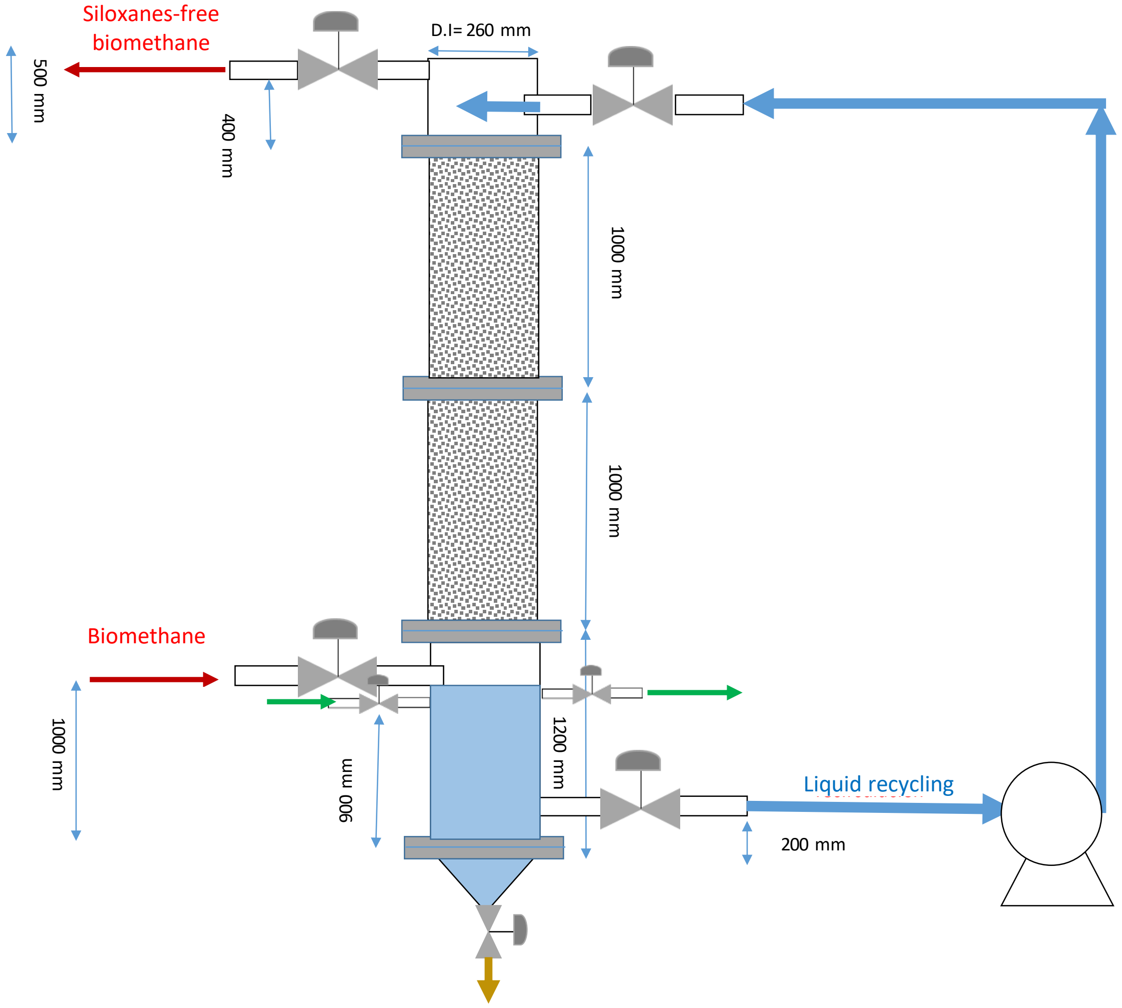

Figure 8.2. Schematic diagram of the biotrickling filter for the removal of siloxanes from biomethane implemented in the URBIOFIN project.

Figure 8.3. Siloxanes removal unit: pilot scale two-phase partitioning biotrickling filter.

The most important design parameters of the pilot-scale BTF are the volume (V) and the bed height (H). A design height of 2 m was selected to maximize the mass transfer of siloxanes from the biomethane to the recycling liquid and to minimize the pressure drop of the biomethane through the packed bed. The packing material chosen for this design was kaldnes k3 rings (Figure 8.4). The EBRT of operation ranged between 55 and 19 minutes. For this purpose, the biomethane flow supplied to the BTF was increased from 2.73 to 8 m^3 d^{-1}. The volume of the recirculating liquid holding tank was 50% of the volume of the packed bed (52 L). The system was operated at outdoor temperature (between 0 and 44 ºC) with no temperature control throughout the experiment.

Figure 8.4. Selected packed material: kaldnes k3 rings.

The TP-BTF was inoculated with the mix of enriched cultures obtained from previous TP-BTFs operated for 177 and 140 days under aerobic and anoxic conditions, respectively, for the removal of VMS (Chapter 6). The most representative active bacteria in the aerobic culture were unclassified members of the order Rhodospirillales (27.2 ± 0.1%), uncultured Proteobacteria of the clade *Acidithiobacillacea* KCM-B-112 (22.6 ± 0.1%) and the genera *Parvibaculum* (11.8 ± 0.2%), followed by the genus *Nocardia* (7.1 ± 0.3%), *Aquamicrobium* (5.4 ± 0.5%) and *Pseudoxanthomonas* (5.2 ± 0.4%). The most abundant active bacteria in the anoxic culture were uncultured members of the family *Phyllobacteriacea* (21.0 ± 0.9%), followed by the genera *Nocardia* (14.8 ± 0.4) and *Baekduia* (12.7 ± 0.4%). The mixture between the silicone oil and the mineral medium was carried out by means of its continuous recirculation from the upper part and the lower part of the nutrient reservoir by using a pneumatic pump, in order to avoid settling due to the different densities between the aqueous mineral medium and the silicone oil. This mixture was continuously recycled to the top of the column by a second pneumatic pump. The pump selection was based on the silicone oil viscosity (270 cSt). The VMS-loaded biomethane stream from a photosynthetic biogas upgrading unit was fed at the bottom of the packed bed countercurrently with the trickling liquid solution (Figure 8.5). The siloxanes-free biomethane stream was conducted to the safety torch.

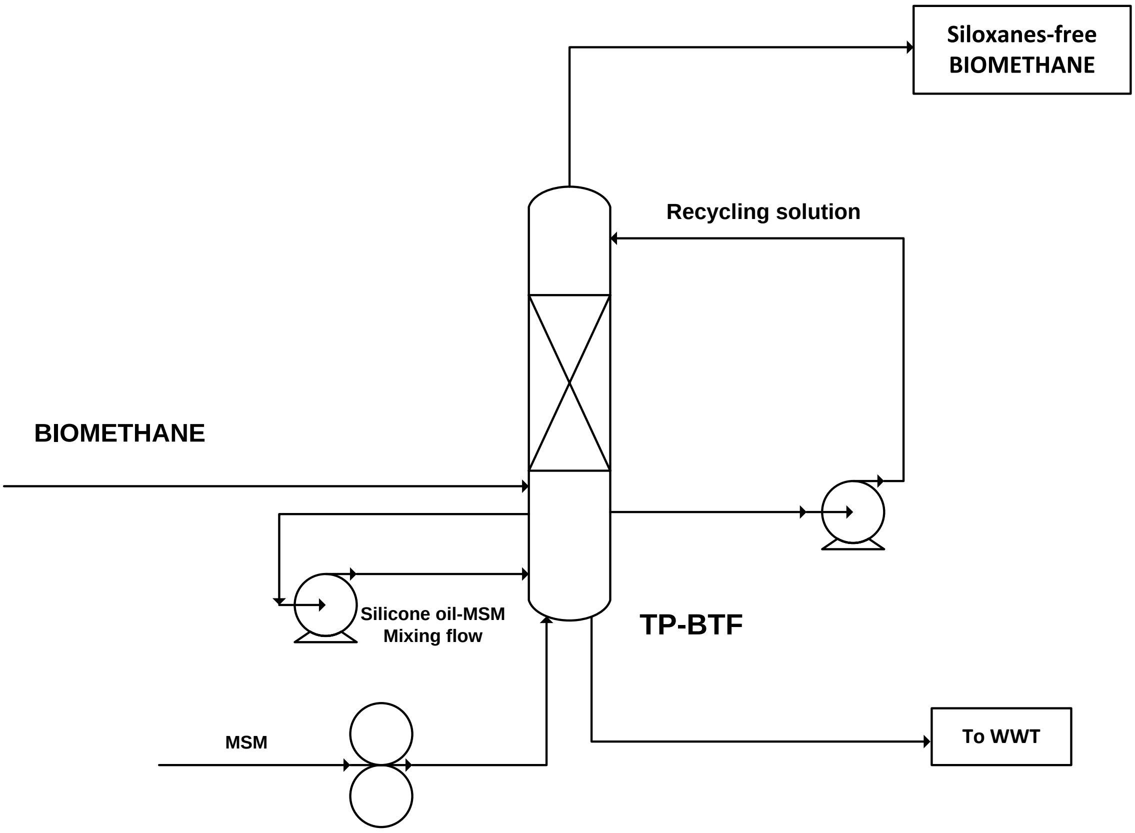

Figure 8.5. Process diagram of a two-phase biotrickling filter for siloxanes removal from biomethane.

Instrumentation for online-monitoring temperature, pressure and flow was installed in the system. During the operation of the pilot-scale TP-BTF, the VMS concentration in the biogas from a two-stage anaerobic digestion system, in the biomethane obtained from the photosynthetic biogas upgrading unit, and in the biomethane obtained from the TP-BTF was measured two times per week in the GC-MS in collaboration with URBASER. The mineral salt medium (MSM) was composed of (g L^{-1}): KH_2PO_4, 0.7; $K_2HPO_4 \times 3H_2O$, 0.92; KNO_3, 3; NaCl, 0.2; $MgSO_4 \times 7H_2O$; $CaCl_2 \times 2H_2O$ 0.026; and 2 $mL.L^{-1}$ of a micronutrients solution containing ($g.L^{-1}$): EDTA, 0.5; $FeSO_4 \times 7H_2O$, 0.2; $ZnSO_4$ ×

$7H_2O$, 0.01; $MnCl_2 \times 4H_2O$, 0.003; H_3BO_3, 0.003; $CoCl_2 \times 6H_2O$, 0.02; $CuCl_2 \times 2H_2O$, 0.001; $NiCl_2 \times 6H_2O$, 0.002; $NaMoO_4 \cdot 2H_2O$, 0.003. The MSM was exchanged according to the nitrate consumption rate. Silicone oil was purchase from COGELSA (200 cSt).

8.4 Main results

The pilot scale TP-BTF was operated for 179 days. During the first 84 days and between 96 and 146 days of operation, the GC-MS available in the facilities was under maintenance, thus the system was not monitored during these periods. During the first stage of the experiment (until day 90), working at a silicone oil fraction of 10%, no significant siloxanes removals were observed when their concentration in both biogas and biomethane was lower than 10 mg m^{-3}. This was associated to the low VMS concentration gradient and the poor mix between the mineral medium and the organic phase (silicone oil) in the trickling solution, which hindered the mass transfer of VMS from the gas phase to the biofilm. From day 90 onwards, two pneumatic pumps recommended for high viscosity fluids were installed in the system to mix and to recycle the liquid solution. The removal efficiency increased up to 47% when the siloxanes concentration increased to 100 mg m^{-3}, corresponding to an inlet load and elimination capacity of 167 and 79 mg m^{-3} h^{-1}, respectively (Figures 8.6 and 8.7). After that, the inlet VMS concentration in both biogas and biomethane dropped again to 10-20 mg m^{-3} (inlet load 30-60 mg m^{-3} h^{-1}) and consequently, both RE an EC decreased and remained between 25-30% and 20-30 mg m^{-3} h^{-1}, respectively. Despite the lower performance of the system, the VMS outlet concentration remained between 9 and 11 mg m^{-3} (around the limit imposed by European legislation of 10 mg m^{-3}).

No significant differences were observed when the silicone oil in the trickling solution was increased to 20% by day 174.

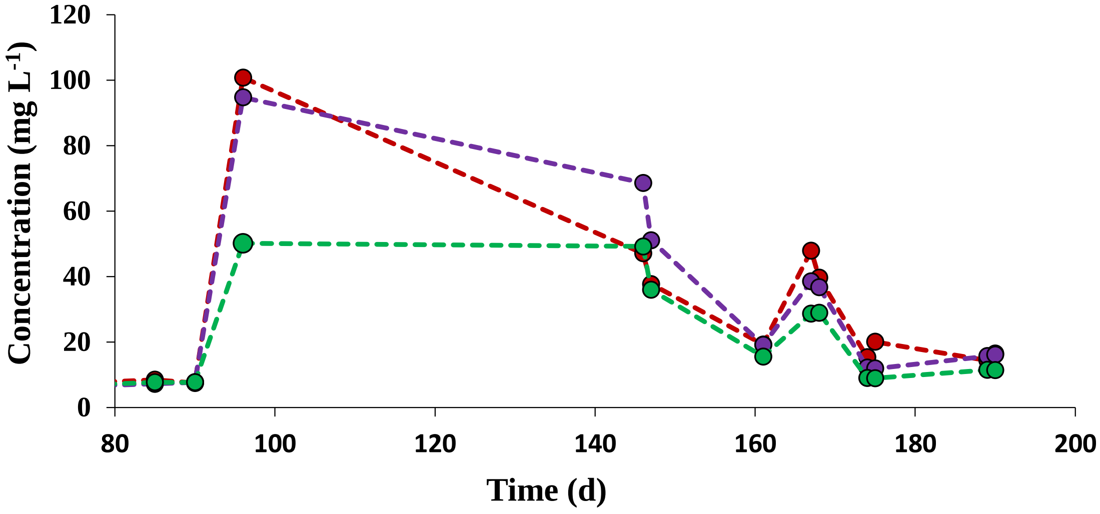

Figure 8.6. Time course of the total VMS concentration in the biogas from the two-stage anaerobic digestion system(●), in the biomethane from photosynthetic biogas upgrading unit (●) and in the biomethane obtained from the pilot-scale TP-BTF (●).

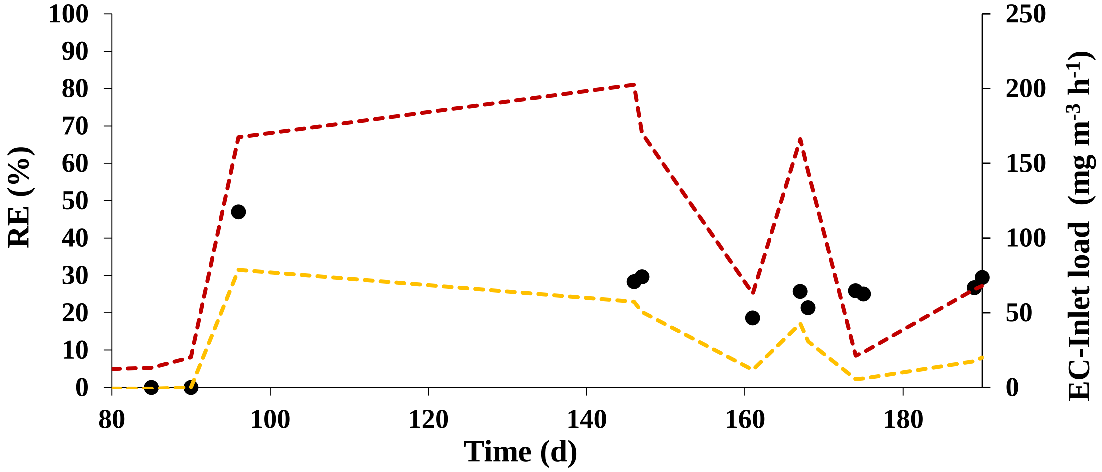

Figure 8.7. Time course of the total VMS removal efficiency (●), inlet load (red dotted line) and elimination capacity (yellow dotted line) in the pilot-scale TP-BTF.

The most abundant siloxanes in the biogas were D4 and D5, representing between 4-30% and 30-94% of the total VMS concentration, respectively, throughout the experiment. As expected, a similar response compared to the total VMS was observed for D5, since it was the dominant compound. D5 RE increased up to 56% when the inlet concentration reached 74 mg m^{-3} (inlet load of 138 mg m^{-3} h^{-1}) and the pneumatic pumps were installed (Figure 8.8). However, no abatement was observed for D4. D5 RE decreased below 40% when the concentration dropped to 20 mg m^{-3}. The performance of the system increased for D4 despite the lower inlet loads and concentrations, remaining at similar RE values as D5. Unlike observed for the total VMS concentration, the increase in the silicone oil content of the trickling solution boosted the abatement of both D4 and D5, reaching the maximum RE values of 67 and 52%, respectively, despite the lower inlet concentration. The maximum ECs achieved were 7 and 20 mg m^{-3} h^{-1} for D4 and D5, respectively, corresponding to final biomethane outlet concentration of 2 and 3 mg m^{-3}.

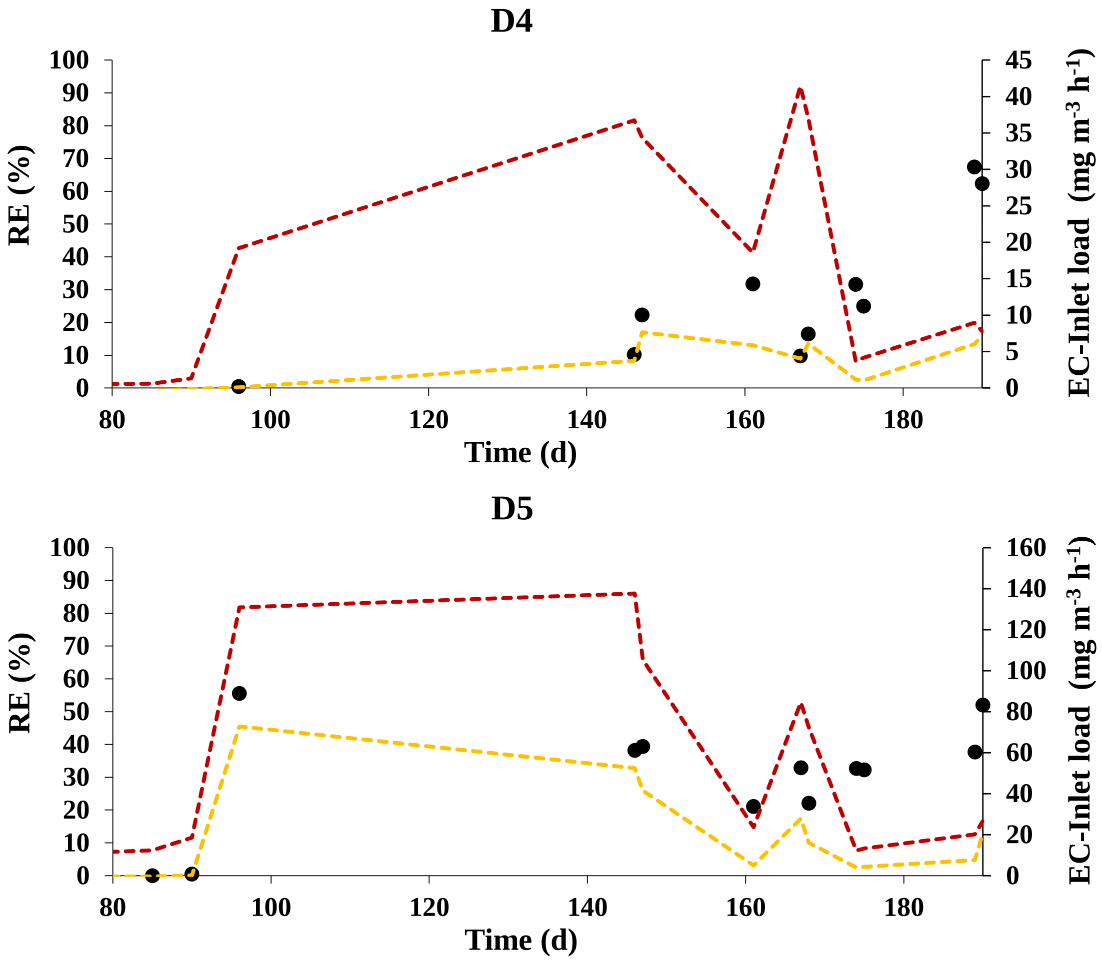

Figure 8.8. Time course of D4 (upper figure) and D5 (bottom figure) removal efficiency (●), inlet load (red dotted line) and elimination capacity (yellow dotted line) in the pilot-scale TP-BTF.

8.5 Conclusions

According to the previous results obtained in lab scale experiments (Chapter 3, 4, 5 and 6), a pilot-scale TP-BTF was designed and constructed in the Waste Technological Innovation Center “Alfonso Maíllo”(CIAM, URBASER) as a polishing step for siloxanes removal from upgraded biogas. The VMS concentration in the biomethane obtained remained above 10 mg m^{-3} independently of the concentration of siloxanes in biogas When the concentration of siloxanes in both, the biogas and the biomethane was lower than 30 mg m^{-3}, siloxanes removal was negatively affected. Nevertheless, siloxanes concentration in the outlet remained between 9 and 11 mg m^{-3} (around the limit imposed by European legislation of 10 mg m^{-3}). D4 and D5 were the most abundant siloxanes in the biogas, representing 4-30% and 30-94% of the total siloxanes, respectively. The maximum removals of both D4 and D5 (67% and 52%, respectively) were recorded during the last operation period, when the silicone oil fraction in the trickling liquid solution increased from 10 to 20%.

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Chapter 9.

Conclusions and future work

In the present thesis, different experiments were carried out in order to study the enhacement of siloxanes removal mediated by the addition of an organic phase to the recirculating nutrient solution of a BTF. The results achieved revealed the feasibility of TP-BTFs as a new and sustainable platform for the abatement of VMS in atmospheric emissions and as a polishing stage in biogas upgrading.

The first finding of this work was the superior performance of two phase partitioning bioreactors in comparison to conventional biofilters, as discussed in **Chapter 3**. In this study it was demonstrated that the removal of VMS increased from 30% in a conventional BTF to 70% in a TP-BTF constructed with 30% of silicone oil under aerobic conditions. Overall, a better performance (~ 90%) was recorded for the cyclic VMS, D4 and D5. The removal efficiency of the linear VMS was lower though. Removals of 20-60% were obtained for L2 and 70-80 % for L3. This finding was related to their higher vapor pressure, which decreases VMS solubility in the organic phase. In order to optimize the performance and the design of the TP-BTF, the main operating parameters (EBRT and silicone oil fraction) were studied in **Chapter 4**. The performance of the system decreased by 27% when the EBRT was reduced from 60 to 15 min, while an increase in the silicone oil fraction by 45% enhanced VMS removal by 17%.

The feasibility of the anoxic biodegradation of the TP-BTF was assessed in **Chapter 5**. The best performance was obtained at a silicone oil fraction of 45% and an EBRT of 1 h. The inferior performance of the system in comparison with aerobic conditions was associated to the lower VMS concentration in the pollutant stream compared to the previous experiments, which reduced the overall gas-liquid VMS mass transfer. Thus, innovative mass transfer strategies were investigated to reduce the mass transfer limitations under both anoxic and aerobic conditions (**Chapter 6**). To this aim, the influence of the trickling liquid velocity and of the internal gas recirculation ratio on the performance of the TP-BTF were studied. An enhancement in the performance of both anoxic and aerobic TP-BTFs was recorded by increasing the TLV from 2 to 10 m h^{-1} (maximum REs around 50%). However, a further increase in the TLV to 20 m h^{-1} negatively affected the bacterial community, likely due to biofilm detachment, resulting in a decrease in the total VMS RE in both TP-BTFs. On the other hand, the internal gas recirculation did not significantly improve the total VMS removal performances compared to the maximum REs previously obtained. In fact, a further increase in the gas recirculation to 3 L min^{-1} negatively affected the operation. This was associated to both the lower VMS inlet concentrations entering the TP-BTF and the excessive turbulence in the surroundings of the biofilm. Interestingly, D5 was scarcely affected by the modifications implemented in the system reaching maximum REs around 74%.

Moreover, this thesis substantially contributed to the study of the biological degradation of siloxanes through the study of the bacterial and archaeal population dynamics in the different experiments. Despite the different inocula used in the conventional BTF and TP-BTF (**Chapter 3**), the DNA sequencing revealed a similar microbial community by the end of operation in both BTFs, with *KMBC-112*, *Reynarella* and *Chitinophaga* as the dominant bacteria under aerobic conditions. This bacterial community was employed as inoculum in **Chapter 4.** A further specialization was observed in this study, finally obtaining a consortium dominated by the clade *Acidithiobacillacea KCM-B-112*. The absence of oxygen affected the specialized dominant population in the TP-BTF as observed in **Chapter** 5. The consortium observed under anoxic conditions was dominated by the genera *Parvibaculum*, *Zarvazinia, clade Acidithiobacillacea KCM-B-112*, *Arenimonas*, *Moraxellaceae* and *Luteimonas* (**Chapter 5**). The RNA analysis performed in **Chapter 6** revealed the active bacterial population according to the transcriptome when siloxanes were the sole carbon source present. This analysis confirmed that the clade

Acidithiobacillacea KCM-B-112 and the genus *Parvibaculum* were among the most active bacterial members under aerobic conditions, while members of the family *Phyllobacteriacea* and the genera *Nocardia* and *Baekduia* dominated the biofilm under anoxic conditions.

Beyond the experimental results obtained, the techno-economic and environmental study performed in **Chapter 7** revealed that, although in a very early stage, emerging biological technologies for siloxanes removal can reduce the environmental impact and operating costs of physical chemical technologies and most likely play a key role on the future abatement of VMS from waste gas streams.

Finally, the TP-BTF was scaled up in the Waste Technological Innovation Center “Alfonso Maíllo” (CIAM, URBASER) (**Chapter 8**). This system was designed to treat biomethane obtained from a photosynthetic biogas upgrading unit. The VMS treatment was successful and complied with the target concentration imposed by the European biomethane Standard of 10 mg VMS m^{-3}.

Despite the substantial contribution and promising results obtained in this thesis on the biological removal of siloxanes, there is still uncover knowledge and room for process optimization. The future research activities in this field should be focused on:

- Further optimization of the TP-BTF configuration: improving the silicone oil-mineral salt medium mixture in the trickling liquid via water-in-oil emulsion techniques (e.g ultrasound technology, surfactant addition, etc.).
- Study of the effect of different package materials on siloxanes removal and biofilm growth, since the affinity of certain materials for siloxanes could improve both the mass transfer and the biomass attachment.

- Assessment of novel mass transfer strategies: gas pre-sparging through the recycling liquid in a pressurized chamber.
- Isolation of the bacteria involved in the biodegradation of VMS for the study of the metabolic pathways involved and characterization of their optimal growth conditions (such as temperature, pH or the necessary micronutrients).
- Evaluation of the influence of the biogas composition in both the bacterial community and the siloxanes removal performance.
- Upscaling to TLR 7 the TP-BTF technology engineered in this thesis

Chapter 10.

About the author

Biography

Celia Pascual Centeno (Valladolid, 1993) studied Chemical Engineering Degree at the University of Valladolid (Spain). She holds a MSc in Environmental Engineering from University of Valladolid (Spain). During her early research career, Celia was involved in several research projects related to the assessment of the performance of bioreactors for the treatment of volatile organic compounds (VOCs). In 2015, Celia collaborated for the first time with the VOC and Microalgae Research Group of the Institute of Sustainable Processes in the anoxic biodegradation of BTEX in a biotrickling filter. In 2016, she was awarded with a collaboration grant in research projects at the University of Valladolid for the treatment of odours and VOCs from wastewater treatment plants and petrochemical industries through compact and highly efficient biological systems. Her research was focused on trimethylamine abatement in algal-bacterial photobioreactors and was supervised by Dr. Raquel Lebrero and Dr. Raúl Muñoz. In 2017, she did the MSc internship in SOCAMEX participating in a Horizon 2020 European project called EnergyWater, within the R&D Department. The purpose of the project was the development of tools to provide support to small and medium-sized companies assessing their consumption in water processes and improving their energy efficiency. Her MSc thesis was focused on the optimization of anoxic desulfurization of biogas via biofiltration. After completing the MSc, she collaborated for 3 months in the project “Elimination of fluorides in molding sands” supervised by Dr. Pedro A. García-Encina and Dr. Rubén Irusta. At the end of 2017, Celia joined the URBIOFIN project as a predoctoral research within the VOC and Microalgae Research Group (Institute of Sustainable Processes - University of Valladolid) to develop her PhD thesis under the Chemical and Environmental Engineering PhD Programme. Her research focused on the removal of siloxanes from biogas and atmospheric emissions in high mass transfer labsale and demo-scale bioreactors. In 2020, Celia developed a 3-month research stay in the Laboratory of Microbiology at Wageningen University. During the stay, she works on the use of bioinformatic tools and genomic databases under the supervision of Dr Irene Sánchez-Andrea.

Publications in ISI-indexed journals

Within the scope of this PhD thesis:

Pascual, C., Cantera, S., Lebrero, R., 2021a. Volatile Siloxanes Emissions : Impact and Perspectives. Trends Biotechnol. 39, 1245–1248. https://doi.org/10.1016/j.tibtech.2021.05.003

Pascual, C., Cantera, S., Muñoz, R., Lebrero, R., 2022. Innovative polishing stage in biogas upgrading: Siloxanes abatement in an anoxic two-phase partitioning biotrickling filter. J. Clean. Prod. 371. https://doi.org/10.1016/j.jclepro.2022.133427

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Out of the scope of this PhD thesis:

Akmirza, I., **Pascual, C.**, Carvajal, A., Pérez, R., Muñoz, R., Lebrero, R., 2017. Anoxic biodegradation of BTEX in a biotrickling filter. Sci. Total Environ. 587–588. https://doi.org/10.1016/j.scitotenv.2017.02.130

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Ángeles Torres, R., Marín, D., Rodero, M. del R., **Pascual, C.**, González-Sanchez, A., de Godos Crespo, I., Lebrero, R., Muñoz R., 2020. Biogas treatment for H2S, CO2, and other contaminants removal, in: From Biofiltration to Promising Options in Gaseous Fluxes Biotreatment. https://doi.org/10.1016/b978-0-12-819064-7.00008-x

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Oral communication

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Víctor Pérez, Cristian A. Severi, **Celia Pascual**, R. Lebrero y R. Muñoz. Proyecto URBIOFIN: Transformación de biogás en biometano a escala piloto. LIFE SMART AgroMobility, 15 July 2021. Soria (Spain).

Raquel Lebrero, **Celia Pascual**, Víctor Pérez, Cristian A. Severi, Raúl Muñoz. Biogas from anaerobic digestion: future prospects for sustainable use and valorization. Water Energy Nexus. 02-04 December 2020. Online

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Víctor Pérez, **Celia Pascual**, Raquel Lebrero, Raúl Muñoz. Transformación de biogás en biopolímeros y biometano a escala semi-industrial. 36 Jornadas Nacionales de Ingeniería Química. 04-04 septiembre 2019. Zaragoza (España)

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Poster communications:

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Celia Pascual, Sara Cantera, Raúl Muñoz, Raquel Lebrero. Comparative assessment of two biotrickling filters for siloxanes removal: effect of the addition of an organic phase. 7ª Jornada de Doctorandos. 02 December 2019. Escuela de Doctorado, University of Valladolid (Spain).

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Participation in Research Projects

Circular Biocarbon (No. 101023280)
Main researchers: Raúl Muñoz, Raquel Lebrero (University of Valladolid)
Funding: Bio-based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme

URBIOFIN project: Urban Biorefinery (Nº 745785).
Main researchers: Raúl Muñoz, Raquel Lebrero (University of Valladolid)
Funding: Bio-based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme

Teaching and Co-supervision/Mentoring

Final year projects:

Co-supervisor of David Antolín Alonso, student of BSc in Chemical Engineering at University of Valladolid. Project title: Eliminación de siloxanos del biogás: estudio comparativo de sistemas físicos y biológicos. Academic year 2021/22. Grade: 9.5

Co-supervisor of Gonzalo Herranz Gómez, student of BSc in Chemical Engineering at University of Valladolid. Project title: Estudio y optimización de un biofiltro percolador anóxico para la eliminación de siloxanos del biogás. Academic year 2019/20. Grade: 9.3

Research internships:

David Antolín Alonso, student of BSc in Chemical Engineering (150 h) 2020/2021)
Ana Herrero Gallardo, student of BSc in Chemical Engineering (150 h) 2019/2020)

Committee membership

Member of the Institute of Sustainable Processes (ISP) of the University of Valladolid since 2018.

Member of the Permanent Committee of the Institute of Sustainable Processes (ISP) of the University of Valladolid since 2018.

Member of the Committee of the MSc in Environmental Engineering from University of Valladolid since 2017.

Reviewer Experience

Reviewer in Journal of Environmental Management - JEMA (IF: 8.628) since 2021.

Reviewer in Journal of Environmental Science & Technology- ES&T (9.516) since 2021.

Reviewer in Journal of Chemosphere (8.943) since 2022.

Specialized Courses and Workshops

“Seminario “¿Cómo realizar una evaluación económica en proyectos de ingeniería?” (4h-online) Escuela de Ingenierías Industriales, University of Valladolid. 24/06/2022.

“Enzimas fúngicas: producción y aplicaciones biotecnológicas” (8h-online). Escuela de Ingenierías Industriales, University of Valladolid. 18 - 21 octubre de 2021.

“Cómo orientar tu carrera académica” (8h-online). Actividades Formativas Transversales de la Escuela de Doctorado, University of Valladolid (EsDUVa). 26 - 27 mayo de 2021.

“Valorización de resultados de investigación y creación de ebts (ciencias, ciencias de la salud, ingenierías y arquitectura).” (6h-online). Parque Científico UVa. 26 - 27 abril de 2021.

“Bibliometría en la evaluación de resultados de la investigación.” (12h-online) Actividades Formativas Transversales de la Escuela de Doctorado University of Valladolid (EsDUVa). 16 - 25 marzo de 2021.

“Introduction to Next-Generation Sequencing Technologies” (5h-online). 10-11 December 2020. Escuela de Ingenierías Industriales. Lecturer: Dr. Sara Cantera (Wageningen University and Research Center, The Netherlands).

“Eficiencia y viabilidad de nuevas tecnologías en procesos de tratamiento de aguas residuales” (10h). 09-13 March 2020. Escuela de Ingenierías Industriales, University of Valladolid. Lecturer: Dr. Francesc Hernández (University of Valencia, Spain).

“Seguridad en el trabajo en laboratorios” (2h-online). Quironprevencion slu. 17 junio 2020.

“Análisis de datos con SPSS (nivel inicial)” (20h). Actividades Formativas Transversales de la Escuela de Doctorado, University of Valladolid (EsDUVa). 10-21 enero de 2020.

“Iniciación al análisis de secuencias 16 S Illumina® MiSeq para el estudio de comunidades bacterianas” (14h). 16-19 December 2019. Escuela de Ingenierías Industriales, University of Valladolid. Lecturer: Dr. Sara Cantera (Wageningen University and Research Center, The Netherlands).

“Curso Inglés (Speaking) B2” (50h) Actividades Formativas Transversales de la Escuela de Doctorado, University of Valladolid (EsDUVa), 11 de marzo -19 de Junio de 2019.

“Curso Inglés (Writing) B2” (50h) Actividades Formativas Transversales de la Escuela de Doctorado, University of Valladolid (EsDUVa), 11 de marzo -19 de Junio de 2019.

“Gas Chromatography basic course” (6h). 14 and 21 of February of 2019. Escuela de Ingenierías Industriales, University of Valladolid. Lecturer: Dr. Jon Sanz Landaluze (Complutense University of Madrid, Spain)

“Curso ATEX - ATmósferas EXplosivas” (2h-online). Quironprevencion slu. 18-22 marzo 2019

“Gestión de la información. Gestores bibliográficos y bibliografía” (20h). Actividades Formativas Transversales de la Escuela de Doctorado, University of Valladolid (EsDUVa), 04 -18 de marzo de 2019.

“Orientación para la búsqueda de empleo en la industria privada” (4,5h). Escuela de Ingenierías Industriales, University of Valladolid. 10-24 julio 2018.

“Orientación para la continuación de la actividad investigadora después de la tesis” (2h). School of Industrial Engineering, University of Valladolid. 19 julio 2018.

“Cómo escribir abstracts y artículos científicos en inglés” (12,5h). Actividades Formativas Transversales de la Escuela de Doctorado, University of Valladolid (EsDUVa), 22 -23 de noviembre de 2018.

Course “Taller práctico sobre Técnicas analíticas físico-químicas e instrumentales” (8.5h) 06-16 November 2018. Escuela de Ingenierías Industriales, University of Valladolid.

“Escritura de artículos científicos en ingeniería y arquitectura” (4h). Actividades Formativas Transversales de la Escuela de Doctorado, Universidad de Valladolid (EsDUVa), 31 de mayo de 2018.

“Curso de Oratoria, Inteligencia Emocional y Programación Neurolingüística (PNL)” (7h). Escuela de Ingenierías Industriales, University of Valladolid. 24 October-07 November. 2017.

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