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

Celia Pascual [a, b], Sara Cantera [c], Raúl Muñoz [a, b], Raquel Lebrero [a, b, *]

[a] Department of Chemical Engineering and Environmental Technology, University of Valladolid, Dr. Mergelina s/n., Valladolid, 47011, Spain
[b] Institute of Sustainable Processes, University of Valladolid, Dr. Mergelina s/n., Valladolid, 47011, Spain
[c] Laboratory of Microbiology, Wageningen University and Research Center, the Netherlands

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ABSTRACT

Biogas contain minor concentration of volatile methyl siloxanes (VMS), responsible for severe damages in turbines or internal combustion engines. Sustainable biological processes for VMS abatement are limited by the low aqueous solubility of VMS. In order this limitation, the siloxanes (D4, D5, L2 and L3) removal performance of a two-phase partitioning biotrickling filter (TP-BTF) was study in terms of the empty bed residence time (EBRT) and the fraction of the organic phase (silicone oil). 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 share 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%. 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 genus *KCM-B-112* was retrieved at the end of the experiment.

1. Introduction

Biogas from the anaerobic digestion of organic waste and landfills represent a promising renewable energy source that can be employed to produce heat and power, as a transport biofuel or as a raw material for further conversion [1]. The number of biogas plants in Europe has increased by 4% in 2019, reaching a total of 18,943 plants with a biogas production of 15.8 billion cubic metres (167 TWh) [2]. In alignment to the European Green Deal target, the biogas market i) contributes to reduce the natural greenhouse gas emissions, ii) replaces fossil fuels as energy sources, and iii) promotes biofertiliser deployment using the digestate as a sustainable alternative to mineral fertilisers.

However, biogas contains minor concentrations of compounds such as H_2O vapor, H_2S, N_2, O_2, volatile siloxanes and halocarbons [1] that reduce the specific calorific value of biogas and cause several damages to internal combustion engines or turbines [3]. Particularly, volatile methyl siloxanes (VMS) represent one of the most detrimental components during biogas combustion since they react with oxygen primarily resulting in the formation of silicon dioxide (SiO_2) [4]. The SiO_2 deposits, known as silica particles, cause erosion and corrosion of the equipment [5], alter the geometry of the combustion chamber and poison the catalysts employed in steam reforming of fuel cells. This causes an increase in the operating costs together with the emission of carbon monoxide and other undesirable compounds such as formaldehyde [6].

VMS are low molecular weight compounds produced as a result of polydimethylsiloxanes (PDMS) hydrolysis, widely used in industrial and domestic applications such as textile manufacturing, construction and cosmetics and personal care products [7]. The most abundant VMS in biogas are hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), D4 contributing to ~ 60% of the total VMS [8]. The concentration of VMS in the raw biogas differs greatly depending on the composition of the organic substrate and the source of biogas (wastewater treatment plants or landfills), with values ranging from 15 up to 400 mg m^{-3} [9]. However, the maximum concentration allowed by regulations for biomethane injection into the natural gas grid is typically 1 mg Si m^{-3} [10]. Consequently, the treatment of the raw biogas to remove

* Corresponding author. Institute of Sustainable Processes, University of Valladolid, Dr. Mergelina s/n., Valladolid, 47011, Spain.
E-mail address: raquel.lebrero@iq.uva.es (R. Lebrero).

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VMS is of utmost importance. Among the commercially available physical-chemical technologies for siloxanes removal from biogas, adsorption on activated carbon and silica gel is the most commonly employed, followed by absorption, cryogenic condensation, catalytic and oxidation processes and membrane separation [11]. Despite the advantages associated to these conventional technologies, such as good abatement performance or robustness, they still face important drawbacks associated to their high energy demand, operating costs and environmental impact.

Albeit scarcely studied, biotechnologies represent a promising alternative for VMS removal due to their higher cost-effectiveness and environmental friendliness [12]. Particularly, biotrickling filtration has been identified as the technology exhibiting the lowest operating costs for siloxanes removal from biogas compared to the above mentioned physical-chemical technologies [13]. In this context, previous studies have evidenced the biodegradation of VMS in biotrickling filters (BTFs) under both anoxic and aerobic conditions [14,15], either as single pollutants or in combination with trace biogas contaminants such as H_2S, hexane, toluene and limonene [16,17]. Nevertheless, maximum VMS removal efficiencies (REs) between 40 and 50% have been achieved due to the limited mass transfer of VMS from the gas phase to the aqueous phase (containing the microbial community responsible for VMS biodegradation), given the high hydrophobicity and low water solubility of these compounds. In this regard, Li et al. (2014) observed an increase in the performance of D4 removal of up to 74% at an empty bed residence time (EBRT) of 13.2 min in a biotrickling filter inoculated with *Pseudomonas aeruginosa S240*, which was associated to the presence of rhamnolipids, organic biosurfactants produced by *Pseudomonas aeruginosa* [18]. Thus, the implementation of two-phase partitioning bioreactors for the removal of VMS represents an unexplored but promising alternative to boost gas-liquid mass transfer. These systems have been widely implemented for the treatment of hydrophobic volatile organic compounds (VOCs), such as hexane or methane. The presence of an additional organic phase in the bioreactor increases the driving force for the mass transfer, and therefore removal, of hydrophobic compounds [19]. Recent advances have demonstrated the superior performance of a two-phase partitioning BTF (TP-BTF) compared to a conventional BTF (without organic phase) for the removal of four model VMS (L2, L3, D4 and D5) under aerobic conditions. Total VMS removal increased from values < 30% in the conventional BTF up to 70% in the TP-BTF, the highest removals being recorded for the cyclic VMS: ~80 and 90% for D4 and D5, respectively [20].

Based on these promising results, this research aimed at assessing the potential of a TP-BTF for siloxanes removal under aerobic conditions with silicone oil as organic solvent. The influence of two operational parameters, the EBRT and the percentage of silicone oil in the mineral salt medium, was studied by gradually reducing the EBRT and increasing the percentage of silicone oil, respectively. In addition, the structure of the bacterial community enriched in the TP-BTF biofilm was analyzed in order to identify the most representative microorganisms involved in siloxanes biodegradation.

2. Materials and methods

2.1. Mineral salt medium

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).

2.2. Experimental setup and operating procedure

The BTF (Fig. 1) consisted of a cylindrical PVC column (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 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 a compressed air stream 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 column.

The recirculation of the MSM-silicone oil liquid mixture was carried out 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 at a linear velocity of 2 m h^{-1}, countercurrently with the VMS-loaded air stream.

An abiotic test was initially performed to rule out the possibility of siloxanes removal by photolysis or adsorption, 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 experimental period was divided in two test series devoted to assess (i) the influence of the EBRT and (ii) the effect of the silicone oil percentage.

2.2.1. Experimental Test Series I: Influence of the EBRT

The BTF was inoculated with an enriched culture obtained from a previous aerobic two-phase partitioning BTF operated for 172 days for the removal of VMS [20]. After inoculation, the system was operated for 122 days in four different stages (Table 1) at a silicone oil percentage of 30% and a total inlet VMS concentration ranging from 700 to 900 mg m^{-3}, corresponding to an inlet concentration of ~100–200 mg m^{-3} for each individual siloxane (L2, L3, D4 and D5). The EBRT was reduced from 60 min (S1.1) to 45 (S1.2), 30 (S1.3) and 15 min (S1.4) in subsequent stages.

2.2.2. Experimental Test Series II: Effect of the silicone oil percentage

The BTF was re-inoculated with the same enriched culture preserved in glycerol and subsequently reactivated in a 1.2 L glass bottle filled with 0.3 L of fresh MSM for 37 days. A mixture of VMS (L2, L3, D4 and D5) was added to the inoculum headspace as the only carbon and energy source at an initial concentration of ~300 mg m^{-3}. The BTF was operated for 124 days in five different stages (Table 2) at an EBRT of 1 h and a total inlet VMS concentration ranging from 700 to 850 mg m^{-3}. The silicone oil percentage was gradually increased from 5 up to 60% in successive stages.

Twice per week, 200 mL of the trickling culture broth were withdrawn (equivalent to a hydraulic retention time of 17.5 days), settled to recover the silicone oil and the liquid phase replaced with fresh MSM prior being returned to the BTF. No additional silicone oil was supplemented during the entire experimental period. The cultivation broth withdrawn was filtered through 0.7 μm and used for the determination of the pH and the total organic carbon (TOC), inorganic carbon (IC), total nitrogen (TN), total silicon (Si), nitrite and nitrate concentrations. VMS and CO_2 gas concentrations were daily analyzed using two gas sampling ports located at the inlet and outlet gas streams of the BTF.

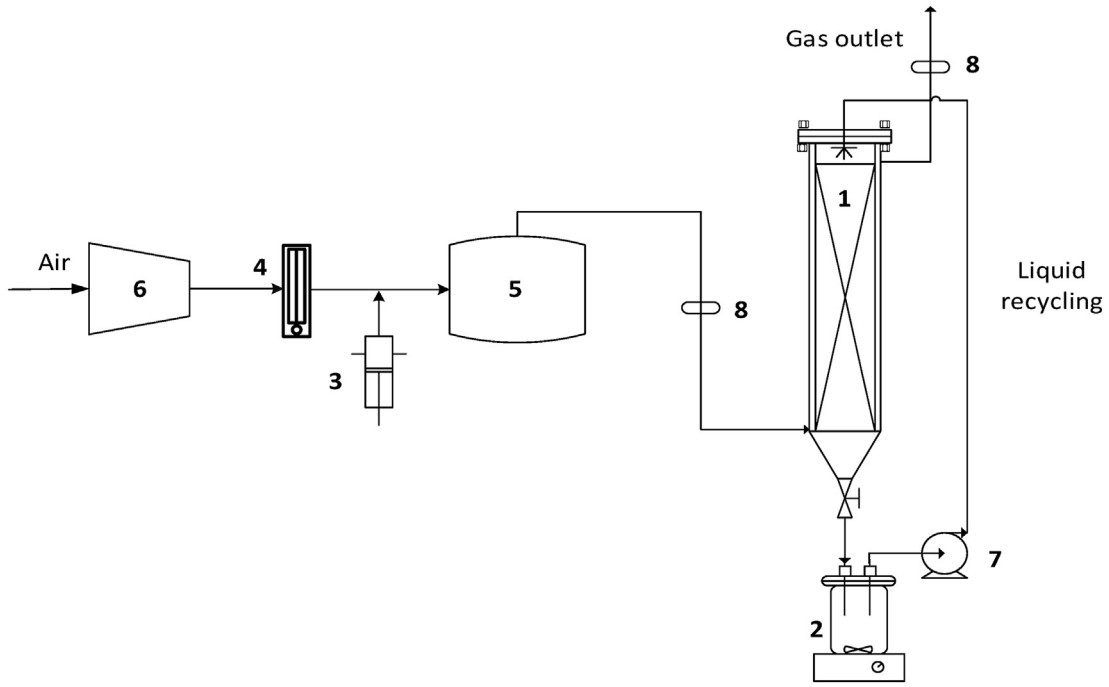

Fig. 1. Schematic representation of the experimental set-up. (1) Biotrickling filter, (2) nutrient reservoir, (3) syringe pump, (4) rotameter, (5) mixing chamber, (6) air compressor, (7) peristaltic pump and (8) gas sampling ports.

Table 1
Experimental conditions during *Experimental Test Series I*.

	EBRT (min)	Elapsed Time (days)	Inlet VMS concentration (mg m^{-3})	Air flow (mL min^{-1})
S1.1	60	0–23	759 ± 122	33
S1.2	45	24–42	705 ± 65	44
S1.3	30	43–73	849 ± 105	67
S1.4	15	74–122	914 ± 106	133

Table 2
Experimental conditions during the *Experimental Test Series II*.

	Silicone Oil (%)	Elapsed Time (days)	Inlet VMS concentration (mg m^{-3})
S2.1	5	0–44	841 ± 73
S2.2	15	45–58	852 ± 85
S2.3	30	59–82	844 ± 81
S2.4	45	83–109	804 ± 62
S2.5	60	110–124	784 ± 76

2.3. Analytical procedure

VMS gas concentration was analyzed in a Bruker 3900 gas chromatograph (Palo Alto, USA) equipped with a flame ionization detector and a HP-5-MS (30 m × 0.25 mm × 0.25 μm) column. Both the detector and injector temperatures were maintained constant at 250 °C. The oven temperature was initially set at 40 °C for 2 min, then increased at 20 °C min^{-1} up to 180 °C, maintained for 1 min and increased again at 20 °C min^{-1} up to 200 °C. Finally, this temperature was maintained for 0.5 min. N_2 was used as the carrier gas at a flow rate of 1 mL min^{-1}. CO_2 and O_2 gas concentrations were 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, respectively, for 5 min. Helium was used as the carrier gas at a flow of 13.7 mL min^{-1}.

The pH of the cultivation broth was determined using a glass membrane electrode 5014 T (Crison, Barcelona, Spain) and a pH-Meter BASIC 20 (Crison, Barcelona, Spain). TOC, IC and TN concentrations were measured in a TOC-VCSH analyzer coupled with a TNM-1 chemiluminescence module (Shimadzu, Japan). Silicon concentration was analyzed by means of an inductively coupled plasma optical atomic emission spectrometer (ICP-OES Radial Simultaneous Varian 725-ES, Agilent). 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 mm × 150 mm) and an IC-Pak Anion Guard-Pak (Waters) according to Muñoz et al. (2013) [21].

2.4. Microbial community analysis

Samples of 20 mL of the inoculum (BTF inoculum) and of the cultivation broth at the end of the *Experimental Test Series I* (BTF_phase1) and *II* (BTF_phase2) of the BTF operation were

withdrawn in duplicate for microbial analysis. The biomass was centrifuged at 13000×*g* for 10 min. The resulting pellet was used for DNA extraction using the MasterPure™ Complete DNA Purification Kit (Epicenter Biotechnologies, USA) according to the manufacturer's instructions. DNA was quantified with Qubit dsDNA broad-range (BR) assays in a QFX Fluorometer (DENOVIX, USA) and subsequently purified. A negative control containing extra pure PCR water was also prepared for analysis (ZymoBIOMICS™ Microbial Community DNA Standard, CA, USA). The extracted DNA (2 biological replicates per sample) was sent for Illumina Miseq amplicon sequencing to the Foundation for the Promotion of Health and Biomedical Research of the Valencia Region (FISABIO, Spain). The sequencing was carried out in duplicate (2 technical replicates) for each biological replicate. For bacterial analysis, amplicon sequencing was developed 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, forward and reverse [22]. For archaeal determination, specific primers for archaea were used (349F S-D-Arch-0349-a-S-17-*GYGCASCAGKCGMGAAW* and 806R S-DArch-0786-a-A-20-*GGACTACVSGGGTATCTAAT*) [23]. Illumina adapter overhang nucleotide sequences were added to the gene-specific sequences. Library construction was carried out using the Nextera XT DNA Sample Preparation Kit (Illumina, San Diego, CA). Libraries were then normalized and pooled prior to sequencing. Samples containing indexed amplicons were loaded onto the MiSeq reagent cartridge for automated cluster generation paired-end sequencing with a 2 × 300 pb paired-end run (MiSeq Reagent kit v3 (MS-102-3001)) according to manufacturer's instructions (Illumina). The 16S rRNA gene sequences were processed using Mothur v1.43.5 following the Mother SOP (https://www.mothur.org/wiki/MiSeq_SOP). Quality filter was performed using Mothur v1.43.5 according to Phandanouvong-Lozano et al. (2018). A second quality filter was conducted with the tools ribosensor, vecscreen, and chimeric search (NCBI Resource Coordinator., 2017) [25] using the GenBank ® genetic sequence database (NCBI, USA). Sequences were then classified into Operational Taxonomic Units (OTUs) using the SILVA 16S rRNA gene reference database (Version: 138). The nucleotide sequence dataset obtained in this study has been deposited at DDBJ/ENA/GenBank as bioproject: PRJNA657479 (https://www.ncbi.nlm.nih.gov/bioproject/PRJNA657479). Prior to diversity analysis, a rarefaction curve was used to determine if each sample was sequenced to a sufficient extent to represent its actual diversity [26]. The rarefaction with 1000 randomizations showed that the smallest representative library was obtained with 15301 reads. Alpha diversity was calculated with the Inverse Simpson Index using Mothur v1.43.5, which quantifies the richness in a community with uniform evenness [24]. Beta diversity among samples was compared by using the Jaccard Index, which measures dissimilarity between two communities based on the taxonomic affiliation and abundance of each OTU [27]. The heat-map of the Jaccard index and the Veen diagrams were developed with Mothur v1.43.5. An analysis of molecular variance (AMOVA) was performed to determine whether the genetic diversity within two or more communities was greater than their pooled genetic diversity and whether the spatial separation among the groups in the Jaccard analysis was statistically significant [28]. The prokariotic community structure was analyzed using R version 3.6.3 (R Core Team, 2019). The main genera of the prokaryotic population is shown in heat-maps plotted using the package *gplots* (R Core Team, 2019) [29].

2.5. Data analysis

The statistical data analysis was performed using SPSS 24.0 (IBM, USA). The results are given as the average ± standard deviation. Significant differences were analyzed by ANOVA and post hoc analysis for multiple group comparisons. Differences were considered to be significant at $p \leq 0.05$.

3. Results and discussion

3.1. Influence of the EBRT

During BTF start-up, large fluctuations in the RE and elimination capacity (EC) were observed for L2, with average values in S1.1 of 45.3 ± 16.5% and 0.07 ± 0.04 g m^{-3} h^{-1}, respectively (Fig. 2 and Figs. S1 and S2). These fluctuations were lower for L3, stabilizing by day 11 at an average RE and EC of 81.1 ± 3.1% and 0.13 ± 0.03 g m^{-3} h^{-1}, respectively. On the contrary, no significant fluctuations in the RE and EC were observed for D4 and D5, reaching average REs of 83.6 ± 1.8 and 87.1 ± 1.4%, respectively, which corresponded to ECs of 0.14 ± 0.03 g m^{-3} h^{-1} for D4 and 0.21 ± 0.02 g m^{-3} h^{-1} for D5 (Fig. 2.B and 2.C).

A significant decrease in the RE was observed for L2, L3 and D4 when the EBRT was reduced from 60 to 45 min during stage S1.2, remaining at average values of 21.4 ± 17.8, 58.2 ± 5.8 and 71.8 ± 6.2%, respectively. Conversely, the removal of D5 was not affected, with steady values of 84.9 ± 2.5%. However, these lower REs entailed statistically similar ECs due to the slight increase in the

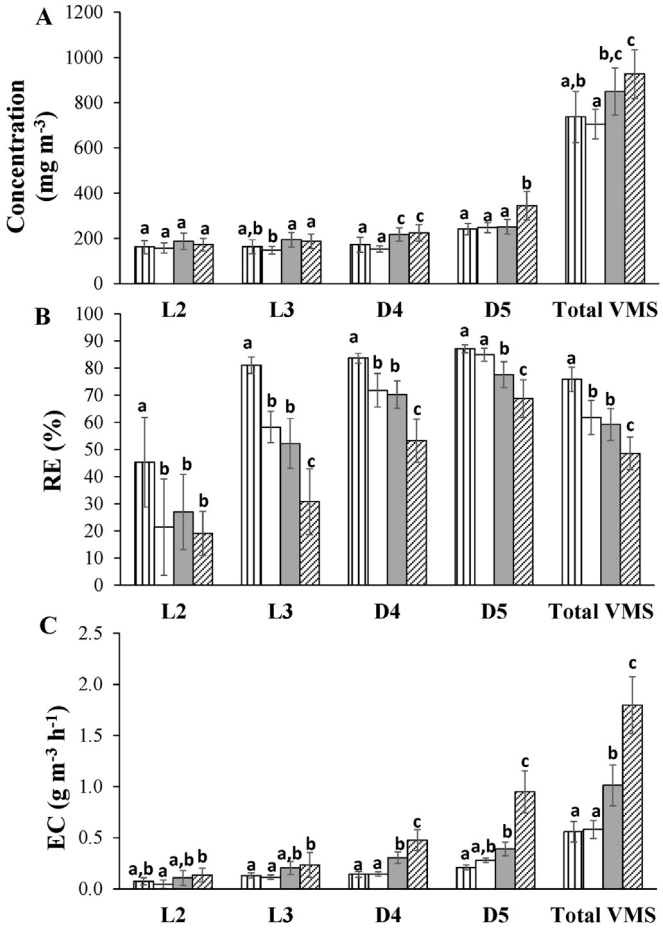

Fig. 2. Average VMS inlet concentration (A), removal efficiencies (B) and elimination capacities (C) in the BTF as a function of the EBRT: 60 min (vertically striped bars), 45 min (white bars), 30 min (grey bars) and 15 min (diagonal striped bars). Vertical lines represent standard deviation from measurements under steady state. Columns within each group with different letters were significantly different at $p < 0.05$ (a, b and c).

VMS inlet load (IL) triggered by the decrease in the EBRT. Thus, average values of 0.05 ± 0.04, 0.12 ± 0.02, 0.15 ± 0.02 and 0.28 ± 0.02 g m^{-3} h^{-1} were recorded for L2, L3, D4 and D5, respectively.

The high removal performance recorded for D4 and D5 supported a further reduction in the EBRT to 30 min during S1.3. Unlike in stage S1.2, no significant differences were observed in the REs of L2, L3 and D4 when the EBRT was decreased from 45 to 30 min, stabilizing at 27.0 ± 13.8, 52.2 ± 9.2 and 70.2 ± 5.1%, respectively. On the contrary, this reduction in EBRT resulted in a detrimental effect in the removal of D5, which decreased to a steady value of 77.5 ± 4.8%. The EC was significantly higher for all VMS in S1.3, with average values of 0.11 ± 0.07, 0.21 ± 0.06, 0.31 ± 0.06 and 0.39 ± 0.07 g m^{-3} h^{-1} for L2, L3, D4 and D5, respectively.

A final reduction in the EBRT to 15 min during S1.4 resulted in a significant deterioration of BTF performance, with a sharp decrease in the RE of L3, D4 and D5 down to 30.8 ± 12.1, 53.2 ± 7.9 and 68.7 ± 7.0%, respectively. Moreover, the RE of L2 slightly decreased to 19.1 ± 8.1% and exhibited large fluctuations as in the previous stages. Overall, a gradual increase in the EC was recorded for all VMS (Fig. S2), with slightly higher values for L2 and L3 (0.14 ± 0.07 and 0.24 ± 0.12 g m^{-3} h^{-1}, respectively) and a significant improvement for D4 and D5 (0.48 ± 0.10 and 0.95 ± 0.20 g m^{-3} h^{-1}, respectively) compared to S1.3. The enhanced EC obtained for D5 compared to the rest of the compounds was associated to the slight increase in the average concentration of D5 in stage S1.4 compared to the other VMS (Fig. 2.A).

The outlet VMS concentration gradually increased as the EBRT was reduced (Fig. S1), reaching minimum average values of 87.4 ± 29.6, 30.8 ± 8.2, 27.9 ± 5.0 and 31.0 ± 2.4 mg m^{-3} for L2, L3, D4 and D5, respectively, at an EBRT of 60 min. Although values close to those required for energy production from biogas (<10 mg m^{-3}) were only achieved for the cyclic VMS, the lower siloxanes concentration expected in raw biogas could ensure the compliance with the maximum limit.

The best abatement performance was obtained for the cyclic VMS, with average REs for D5 slightly higher compared to those recorded for D4 (i.e. 15 % and 23% higher during stages S1.2 and S1.4, respectively). Moreover, the REs achieved during S1.1 for the cyclic VMS were higher than those reported in previous biodegradation studies. For instance, maximum D4 REs ~60% were reported by Wang et al. (2014) [30], while Li et al. (2020) reached a removal of 72% for this VMS in a BTF inoculated with *Pseudomonas Aeruginosa* [18]. Santos-Clotas et al. (2019) observed a maximum steady RE of 45% for D5 in a BTF when 20% of activated carbon was added to the packing material [16]. Similarly, Zhang et al. (2020) recorded a D5 removal of 52%, although this abatement was associated to chemical absorption in the acidic recycling liquid [17].

On the contrary, lower REs were achieved for the linear VMS, L2 and L3, the former exhibiting the lowest abatement performance. Thus, although a RE ~80% was obtained for L3 during S1.1, comparable to that of D4 and D5, values as low as 30% were recorded in subsequent stages. Similarly, L2 REs decreased from ~45% during S1.1–20% during stage S1.2, and remained at similar values throughout the rest of the experiment. The inferior performance recorded for L2 was attributed to its higher vapor pressure compared to the rest of the compounds (4.12 kPa at 25 °C), which limits the solubility of L2 in the organic phase and could also promote its desorption (Rojas Devia and Subrenat (2013) demonstrated the lower mass transfer of siloxanes with higher vapor pressure from the gas phase into different oils [31]).

Overall, the total VMS removal decreased when decreasing the EBRT, reaching steady state values of 75.8 ± 4.5, 61.8 ± 6.3, 59.2 ± 5.8 and 48.6 ± 6.0% in stages S1.1, S1.2, S1.3 and S1.4, respectively. Nevertheless, the EC gradually increased from 0.56 ± 0.10 to 0.58 ± 0.09, 1.01 ± 0.20 and 1.80 ± 0.28 g m^{-3} h^{-1} during stages S1.1, S1.2, S1.3 and S1.4, respectively, which clearly shows that the system was limited by mass transfer and not by biological activity. Similar results were obtained by the authors in a previous work conducted in a TP-BTF operated under the conditions described in stage S1.1: REs of 80–90% for D4 and D5, 70–80% for L3 and 20–60% for L2 [20]. Thus, a clear influence of the EBRT in the abatement of VMS was observed, with a reduction of ~36% of the total removal performance when comparing stages S1.1 and S1.4. This detrimental effect was more remarkable for L2 and L3, which REs were reduced by ~60%.

Previous studies have also reported a deterioration in the performance of VMS abatement when decreasing the EBRT. For instance, Wang et al. (2014) reached the maximum RE for D4 (60.2%) operating at 24 min, decreasing to close to zero values when the EBRT was reduced to 2 min [30]. In the present work, maximum D4 removals of 91.8% were achieved, although at the expenses of a higher EBRT of 60 min. Similarly, Santos-Clotas et al. (2019) observed a decrease in D5 abatement from 37 to 16% when the EBRT was reduced from 14.5 to 4 min [16]. In this context, the EBRT has been consistently identified as one of the most important operational factors influencing the mass transfer from the gas phase to the biofilm and therefore, the removal performance of the BTFs [32]. It is important to remark that, although these EBRTs are considerably higher than those commonly used in BTFs devoted to waste gas treatment, the polluted air flowrates are at least one order of magnitude higher than biogas flowrates, and thus the higher EBRT will not result in comparatively larger bioreactor volumes. Despite the superior VMS abatement performance achieved at higher EBRTs, this parameter should be maintained as low as possible to facilitate the cost-competitiveness of process scale-up.

3.2. Effect of the silicone oil percentage

The recycling liquid (5% silicone oil, 95% MSM, v/v) was completely renewed in the BTF after completion of Experimental test series 1. In this context, high REs and ECs were achieved during start-up likely due to the absorption of the VMS in the fresh silicone oil (Figs. S3 and S4). These values gradually decreased and stabilized by day 27. The highest RE was achieved for D5 with an average steady value of 58.3 ± 4.0%, corresponding to an EC of 0.16 ± 0.02 g m^{-3} h^{-1}. Significantly lower REs were recorded for L2, L3 and D4, with average values of 23.9 ± 12.2, 21.2 ± 12.1 and 26.2 ± 7.9%, respectively. Accordingly, lower ECs of 0.06 ± 0.03, 0.04 ± 0.03 and 0.05 ± 0.02 g m^{-3} h^{-1} were obtained for L2, L3, and D4, respectively (Fig. 3).

A significant increase in the RE was observed for D4 during S2.2 when the percentage of silicone oil in the trickling solution was increased from 5 to 15%, reaching average values of 52.6 ± 8.7%. Since the VMS concentration was maintained roughly constant throughout the entire experiment, the EC values for D4 concomitantly increased up to and 0.38 ± 0.10 g m^{-3} h^{-1}. Nevertheless, the increase in silicone oil percentage did not significantly affect the REs of L2, L3 and D5, which remained at 19.4 ± 14.1, 37.1 ± 9.4 and 59.9 ± 3.2%, respectively (corresponding to ECs = 0.05 ± 0.04 g m^{-3} h^{-1} for L2, 0.28 ± 0.10 g m^{-3} h^{-1} for L3 and 0.15 ± 0.01 g m^{-3} h^{-1} for D5).

Based on the positive effect observed for D5 abatement, the silicone oil percentage was further increased to 30, 45 and 60% in the subsequent stages. An improved removal performance was observed during S2.3, with REs increasing up to 45.8 ± 3.2, 58.8 ± 2.8 and 71.2 ± 3.5% for L3, D4 and D5, respectively, corresponding to ECs of 0.08 ± 0.01, 0.10 ± 0.01 and 0.16 ± 0.01 g m^{-3} h^{-1} (Fig. 3.B and 3.C). Similarly, the RE of the cyclic VMS slightly increased in S2.4, achieving steady values of 64.7 ± 4.1% for D4 and

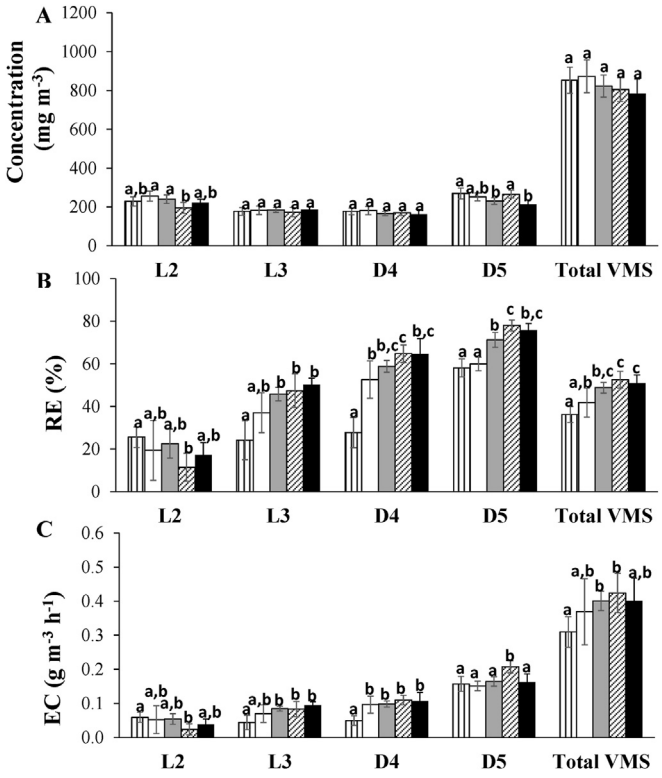

Fig. 3. Average VMS inlet concentration (A), removal efficiencies (B) and elimination capacities (C) in the BTF operated with silicone oil percentages of 5% (vertically striped bars), 15% (white bars), 30% (grey bars), 45% (diagonal striped bars) and 60% (black bars). Vertical lines represent standard deviation from measurements under steady state. Columns within each group with different letters were significantly different at $p < 0.05$ (a, b and c).

78.0 ± 2.6% for D5. However, the last increase in the silicone oil percentage from 45 up to 60% did not trigger any effect in the removal of these VMS, remaining at similar values of 64.5 ± 7.4 and 75.9 ± 3.1% for D4 and D5, respectively (corresponding to ECs of ~0.11 and 0.16 g m^{-3} h^{-1}, respectively). A slight enhancement of the L3 removal performance was recorded during stages S2.4 and S2.5. In this sense, the average REs and ECs increased to 47.4 ± 8.0% and 0.08 ± 0.02 g m^{-3} h^{-1} during S2.4 and to 50.2 ± 3.1% and 0.09 ± 0.01 g m^{-3} h^{-1} during S2.5. Finally, no statistically significant effect of the addition of silicone oil to the trickling solution of the BTF on the removal of L2 was observed, whose values remained at 22.6 ± 6.8, 11.4 ± 6.6 and 17.2 ± 5.7% during stages S2.3, S2.4 and S2.5, respectively (corresponding to ECs of 0.05 ± 0.02, 0.02 ± 0.02 and 0.04 ± 0.02 g m^{-3} h^{-1}). Overall, the outlet VMS concentration gradually decreased as the silicone oil percentage was increased (Fig. S3). Minimum outlet concentrations were achieved when working with 30 and 45% of silicone oil, with average values of 177.6 ± 14.9, 91.7 ± 10.7, 58.0 ± 5.9 and 54.5 ± 4.8 mg m^{-3} for L2, L3, D4 and D5.

As expected, the highest REs were obtained for the cyclic VMS, with a lower abatement performance being recorded for the VMS with higher vapor pressure. On the other hand, the total VMS removal gradually increased from stage S2.1 (5% silicone oil) to stage S2.4 (45% silicone oil), reaching steady state values of 34.6 ± 7.4, 41.8 ± 6.8, 48.8 ± 2.5 and 52.4 ± 4.4 in the subsequent stages. Similarly, the total VMS EC increased from 0.29 ± 0.08 g m^{-3} h^{-1} at stage S2.1 up to 0.42 ± 0.06 g m^{-3} h^{-1} at S2.4.

Overall, a clear influence of the silicone oil percentage in the trickling solution was observed when increased from 5 to 45%. A higher non-aqueous/aqueous phase ratio allows for an increase in the interfacial area involved in mass transport, thus improving the mas transfer of siloxanes from the gas phase to que liquid phase, as indicated in Equation (1).

$$F_{G/W} = K_L^{G/W} a \left(\frac{C_G}{H_{G/w}} - C_w \right) \quad (1)$$

Where $F_{G/W}$ represents the volumetric pollutant mass transfer rate (g m^{-3} h^{-1}), $K_L^{G/W}a$ is the overall volumetric mass transfer coefficient (h^{-1}), C_G and C_W are the pollutant concentrations (g m^{-3}) in the gas and aqueous phase, respectively, and $H_{G/W}$ the dimensionless Henry's law constant.

According to Eq. (1), mass transfer of gaseous pollutants from the gas to the aqueous phase depends on the concentration gradient available for mass transport, which is in turn determined by the dimensionless Henry's law constant of the target pollutant ($H_{G/W}$, so-called gas-water partitioning coefficient) [33]. $H_{G/W}$ values in the order of ~100 have been reported for siloxanes, which are up to 6 orders of magnitude higher than those of water soluble compounds [34,35]. These high values decrease the global concentration gradient, and therefore, the volumetric pollutant mass transfer rate. On the contrary, the partition coefficient air/silicone oil ($H_{G/SO}$) for hydrophobic pollutants can be up to 4000 times lower compared to that of air/water, boosting their concentration gradient in TP-BTFs [36]. For instance, the partition coefficient of hexane decreases from ~70 in water to ~0.0058 in silicone oil [37]. Unfortunately, to the best of our knowledge, the $H_{G/SO}$ values for VMS remain to be determined.

On the contrary, the increase in the silicone oil percentage from 45 to 60% did not affect siloxanes removal. Similarly, previous studies have found a maximum silicone oil/aqueous phase ratio above which a further addition of silicone oil did not result into an enhanced abatement performance. For instance, Ascón-Cabrera et al. (1995) assessed the effect of the silicone oil/aqueous phase ratio in the interfacial area, achieving the maximum value at 30% of silicone oil within the tested range of 8.3–83% [38]. Lebrero et al. (2014) also observed that an increase in the silicone oil percentage from 10 to 20% did not improve the hexane abatement in a TP-BTF, which was attributed to a harmful effect of the silicone oil on the packing material and therefore a reduction of its water holding capacity [19].

3.3. Short-term fate of carbon

The biodegradation of the VMS was also monitored by CO_2 production throughout the entire experiment. During the *Experimental Test Series 1*, no direct correlation between the VMS EC and the CO_2 production was observed. In this sense, the average CO_2 production reached steady values of 3.7 ± 0.2, 2.2 ± 0.3, 4.6 ± 1.1 and 2.2 ± 1.0 g m^{-3} h^{-1} in S1.1, S1.2, S1.3 and S1.4, respectively (Fig. S5.A). Thus, the highest CO_2 production was recorded in S1.3, while the highest total VMS EC was achieved in S1.4. This lack of correlation was attributed to an additional CO_2 production resulting from the degradation of cell debris and death biomass from the bacterial culture during the initial adaptation period. On the contrary, during the second experimental phase, the average CO_2 production increased concomitantly with the increase in the total VMS EC, reaching steady values of 2.2 ± 0.8, 5.3 ± 0.3, 5.7 ± 0.6, 6.0 ± 0.2 and 6.1 ± 0.4 g m^{-3} h^{-1} in stages S2.1, S2.2, S2.3, S2.4 and S2.5, respectively (Fig. S5.B).

Both TOC and Si concentration followed a similar trend throughout the entire experiment, which suggested that the TOC concentration in the cultivation broth was related to dissolved siloxanes or secondary metabolites, such as dimethylsilanediol and/

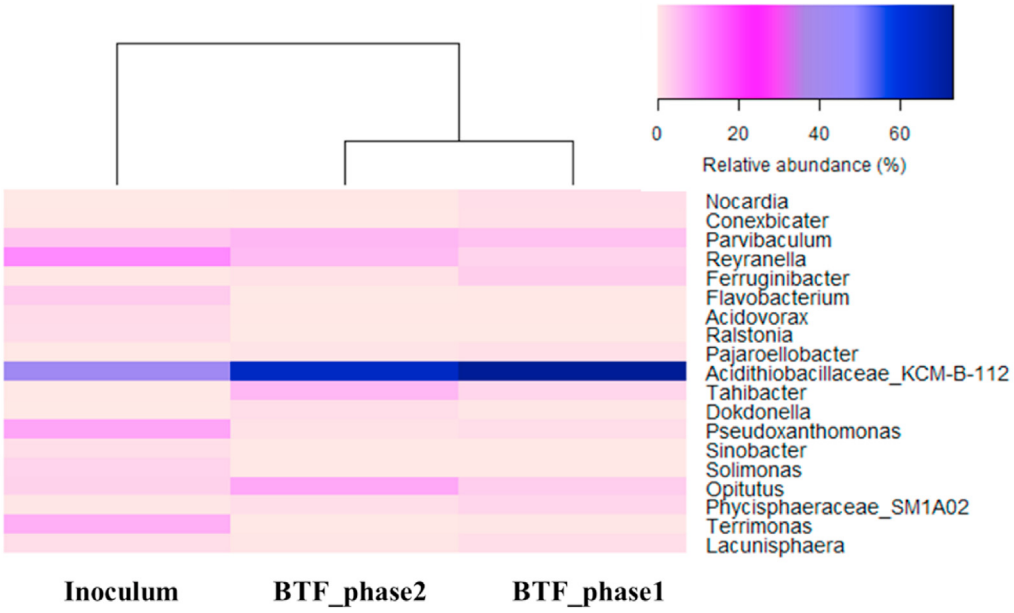

Fig. 4. Heat map showing the differential relative abundance of the most representative genus 53 OTUs during BTF operation. OTUs with relative abundances <0.5 were not included in the data analysis. The dendrogram on top represents hierarchical clustering of the sample points. Data is presented as relative abundance per sample (%).

or silicic acid [18,30]. The TOC concentration in the cultivation broth progressively increased during stages S1.1 and S1.2, reaching a maximum value of 115 mg L^{-1} by day 41 (Fig. S6.A). Afterwards, a reduction in the TOC concentration was observed, stabilizing at 39 ± 7 mg L^{-1} from day 64 onwards. This reduction in the organic carbon concentration corresponded to the increase observed in the CO_2 production, which was associated to the activation of bacteria capable of degrading the dissolved secondary metabolites. Similarly, the total Si concentration increased up to 10.1 mg L^{-1} by day 41 and then stabilized at 2.1 ± 0.4 mg L^{-1} from day 64. It is important to highlight that the MSM replacement rate was maintained constant throughout the entire experiment.

Similar to the CO_2 production, the TOC and Si concentration in the trickling solution increased throughout the stages of the second experimental phase as the percentage of silicone oil was increased. The highest concentrations were recorded during S2.5 with maximum values of 258 and 7.4 mg L^{-1} for the TOC and total Si, respectively, by day 121 (Fig. S6.B). This was attributed to an enhanced mass transfer of silicone compounds due to the increase in the silicone oil percentage, which boosts a secondary path for the transport of VMS from the gas phase to the liquid phase via the silicone oil, thus improving their global mass transfer [39].

3.4. Prokaryotic diversity and community structure

The 16S rRNA gene sequence analysis of the prokaryotic population present in the TP-BTF revealed the presence of 332550 sequences that belonged to a total of 1493 OTUs affiliated with bacterial genera. No archaeal representatives were detected neither using universal primers nor specific primers for archaea (349F-806R). Bacterial richness did not differ significantly between samples according to the alpha diversity analysis (Fig. S7). Indeed, from the total species detected (132), BTF_phase1 (83 total species) shared more than 70% of the species with BTF_phase2 (95 total species) and more than 60% with the inoculum (84 total species) (Fig. S8). This fact can be explained by the long enrichment period of the inoculum used and indicates a direct correlation between the organisms found and biological siloxane degradation. Similar studies have observed a drastic shift to a less diverse and more specialized community when treating siloxanes [17,20,40], and therefore, lower bacterial diversities in comparison with bacterial enrichments treating less complex compounds [24].

On the other hand, bacterial beta diversity was significantly higher in the inoculum (AMOVA, $p < 0.05$), which supported that the inoculum had a similar number of OTUs than those detected after BTF operation, but the OTUs found were more even in the inoculum (Fig. S9). The main representatives of the inoculum belonged to the phylum Proteobacteria, such as representatives of the uncultured genus *Acidithiobacillaceae_KCMB-112* (35.3 ± 5.2%), the genus *Reyranella* (10.1 ± 2.5%), *Pseudoxanthomonas* (7.0 ± 3.1%) and *Parvibaculum* (4.1 ± 0.5%). The other most represented phyla were Bacteroidetes (*Terrimonas* 6.8 ± 1.8% and *Flavobacterium* 3.8 ± 0.9%) and Verrucomicrobia represented mainly by the genus *Opitutus* (2.6 ± 1.8%) (Fig. 4).

The population shifted towards a more specialized bacterial community during BTF operation at the end of *Experimental Test Series I*. The bacterial community was then dominated by representatives of the genus *KCM-B-112*, which constituted 73.0 ± 0.9% of the population. To a lesser extent, some Alphaproteobacteria representatives from the genus *Parvibaculum* (4.6 ± 0.3%) and the genus *Reyranella* (2.5 ± 0.05%) were identified in this stage. Moreover, the population of Bacteroidetes and Verrucomicrobia were dominated in this stage by *Ferruginibacter* (3.2 ± 0.3%) and *Opitutus* (3.3 ± 1.8%), respectively. The increase in the silicone oil content by 30% barely shifted the bacterial population. Hence, after 124 days of operation (end of *Experimental Test Series II*), *Acidithiobacillaceae_KCMB-112* remained dominant (65.3 ± 0.2% of the community). The verrucomicrobial genus *Opitutus* (7.6 ± 0.1%), the alphaproteobacteria *Parvibaculum* (5.8 ± 0.1%) and *Reyranella* (5.4 ± 0.3%), and the gammaproteobacteria *Tahibacter* (5.7 ± 1.5%) were also representative (Fig. 4).

Despite the microbiology involved in siloxanes degradation has been scarcely investigated, the genus *Pseudomonas* has been frequently identified as the most plausible organism able to degrade complex silicone compounds [15,18,41]. However, no species of the genus *Pseudomonas* were found in the present study. Similarly, in previous enrichments using D4 and D5 as the main carbon source and sewage as the inoculum [17,20,40], the main

organisms enriched during VMS biodegradation were not identify as *Pseudomonas* species. Boada et al. (2020) reported a new species of the genus *Methylibium* to be the most efficient D4 degrader [40]. Pascual et al. (2020) obtained a similar consortium to the one enriched in this study using D4 and D5 as the only carbon and energy source. This consortium was dominated by the genera *Pseudoxanthomonas* (3–21%), *Reyranella* (8–10%), *Chitinophaga* (5–7%), *Flavobacterium* (2–11.2%) and a recently discovered uncultured genus from the family *Acidithiobacillaceae, KCMB-112* (7–20%) [20]. Zhang et al. (2020) enriched a prokaryotic population highly dominated by the archaeal genus *Ferroplasma* (85.5%), and the bacterial genus *Acidithiobacillus* (9.5%) in a reactor devoted to the simultaneous removal of siloxanes and H_2S [17]. However, in Zhang's study the members of the genus *Acidithiobacillus* were related to the removal of H_2S, and not to the degradation of siloxanes. The present study determined a member of the family *Acidithiobacillaceae* as the main bacterial genus in a consortium that efficiently removed siloxanes up to values of 80%. This uncultured genus (*KCMB-112*) has been found at urban deposits and also in contaminated soils where the pH was neutral or slightly alkaline, and H_2S was not detected [42]. More research about *Acidithiobacillaceae KCMB-112* should be conducted, with the main objective of isolating novel species of this genus, and carefully studying their capability to degrade siloxanes, as well as their taxonomic affiliation.

4. Conclusions

The influence of two key operating parameters on siloxanes abatement performance in a two-phase partitioning BTF was evaluated: the EBRT and the organic phase percentage. A clear negative influence of the decrease in EBRT on the total VMS removal was observed, decreasing from 76% down to 49% when this parameter was reduced from 60 to 15 min. Among the VMS, satisfactory REs were achieved for the cyclic VMS, D4 (53– 84%) and D5 (69– 87%), while the detrimental effect of the decrease in EBRT on the abatement performance was more remarkable for the linear VMS, L2 (19–45%) and L3 (31– 81%). Conversely, the positive effect of increasing the organic phase resulted in the improvement of the total VMS removal from 35 to 52% when silicone oil percentage in the trickling solution was increased from 5 to 45%. This enhancement was observed for L3 (21–50%), D4 (26–64%) and D5 (58–78%). However, no effect was recorded in L2 abatement, whose REs remained lower than 25% throughout the entire experiment. This inferior performance was associated to its lower solubility in the organic phase due to the higher vapor pressure and the likely formation of L2 as an intermediate metabolite of D4 degradation. CO_2 production, and the presence of dissolved TOC and Si in the cultivation broth confirmed VMS biodegradation throughout the entire experiment. Although a lower removal performance was obtained compared to physicochemical technologies for siloxanes abatement, these results certainly encourage further optimization of this novel generation of high-mass transfer, low cost and sustainable biotechnologies. Finally, the removal of VMS resulted in a highly specialized bacterial community dominated by the genus *KCM-B-112,* which represented ~70% of the population.

CRediT authorship contribution statement

Celia Pascual: Investigation, Formal analysis, Writing – original draft. **Sara Cantera:** Formal analysis, Writing – original draft. **Raúl Muñoz:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Raquel Lebrero:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.renene.2021.05.144.

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