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# Multi-channel capillary bioreactor for hydrophobic VOC and $CO_2$ abatement – Process intensification through silicone oil addition

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ABSTRACT

A multi-channel capillary bioreactor devoted to the continuous abatement of hydrophobic volatile organic compounds (VOCs) by a bacterial and bacterial/microalgae consortium was investigated for 200 days. Toluene, α-pinene and hexane removal in the capillary bioreactor was up to 99 %, 98 %, and 55 %, respectively, which is remarkably high considering the low gas contact time of less than 1 second. Addition of silicone oil increased the removal efficiency (RE) of α-pinene within two days from 45 ± 6 % to 98 ± 2 %, probably through alleviation of biokinetic inhibition provided by the oil acting as buffer for the α-pinene and/or its metabolites. The RE of toluene increased after silicone oil addition over a period of about eight weeks from 81 ± 3 % to 99 ± 1 %, most likely via microbial adaptation. On the contrary, the removal of hexane did not increase following silicone oil addition, potentially due to the inhibition of hexane or its metabolites as the bioreactor was deliberately operated without replenishing the recirculation liquid. Interestingly, biomass adhered to the silicone oil phase rather than residing in the water phase. The bacterial diversity was substantially enhanced, and probably contributed to the observed stable performance of the capillary bioreactor. After the introduction of microalgae on day 150, lower $CO_2$ concentrations at the outlet compared to the inlet were observed immediately. A net $CO_2$ consumption was recorded, achieving complete carbon sequestration from the removed VOCs, along with additional $CO_2$ removed from the inlet ambient air.

## 1. Introduction

Traditionally, physical-chemical technologies have been used to abate gaseous pollutants because of their relatively small size (low gas contact times), rapid start-up (which allows for intermittent operation), and extensive experience in both design and use. Yet, biological processes are now generally recognized as a reliable and economical alternative for the abatement of waste gases containing mostly hydrophilic pollutants and low concentrations [1–4]. Moreover, the growing emphasis on sustainability and process safety is often an important driver for the application of biological air purification processes as they are operated at ambient temperatures/pressures with minimum environmental impact.

Nonetheless, biological gas treatment processes are inherently constrained by the mass transfer of hydrophobic gaseous pollutants. Pollutants with a large dimensionless Henry's law coefficient ($H_{G/W}$) (>0.10 at 25 ºC) are normally limited in terms of mass transfer as their poor solubility in water, especially at low concentrations, decreases their availability in the biofilm phase or the aqueous phase containing cells. Indeed, the high hydrophobicity of VOCs requires long gas contact times that demand large reactor footprints and limit their cost-effective abatement in biological processes [2,3].

Enhancing mass-transfer from the gas phase to a liquid containing micro-organisms typically entails an increase in power consumption (e.g., to enhance mixing), while power consumption is a key parameter for economically sustainable applications. Capillary reactors operated at an explicit gas-liquid flow pattern can create in small (capillary) channels an internal liquid circulation that enhances mass transfer by the short-distance transport mechanism. This segmented gas-liquid flow pattern, also known as Taylor flow or bubble-train flow, consists of alternating liquid slugs and gas bubbles, which enhances mass-transfer and has been reported to yield superior heat and mass transfer rates [5,6]. Moreover, capillary forces are dominant in the capillary channel over other forces as such gravity and viscosity, which result in minimum pressure drop

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requiring minimum energy to move the air and liquid through the channels [7,8]. Capillary reactors have gained interest for process intensification due to both their enhanced mass-transfer and improved reaction kinetics [6,7,9]. In the last decade, thanks to the rapid progress in the integration of microfluidic devices and miniaturization technology, the application of capillary channel microreactors to intensify chemical and biocatalytic processes has increased significantly [5,6,10–12]. Unfortunately, studies on capillary gas-liquid reactors that involve biological conversions to abate gaseous pollutants are scarce [13,14] and primarily deal with single channels.

Furthermore, microbial inhibition due to load surges or sudden changes in operating conditions can also hinder the performance of bioprocesses. Water-immiscible liquids known as non-aqueous phase liquids (NAPLs) were initially used in the production process of products of commercial significance to promote microbial bioconversions of inhibiting or hydrophobic substrates. Biological gas treatment processes using a NAPL added to the aqueous medium have emerged over the last decade as a platform to overcome microbial inhibition by interfering substrates or metabolites [15–17]. A NAPL may also be used as a buffer against load surges or sudden changing operating conditions or against periods of starvation by serving as a reservoir [18]. In addition, a NAPL may enhance the mass transfer pathway for hydrophobic pollutants in a biological gas treatment reactor constrained by the mass transfer that would demand high gas contact times and associated large reactor volumes and footprints [15,16]. Different studies proved that the addition of a NAPL can increase the removal efficiency of hydrophobic VOCs in bioreactors [19–22]. The objective of this study was to investigate the effect of silicone oil as a NAPL on the overall performance and continuous operation of a multi-channel capillary bioreactor treating hydrophobic air pollutants. Toluene, α-pinene, and hexane were used as model compounds, representing indoor air pollutants different in hydrophobicity and biodegradability. Low VOC concentrations ($< 5$ mg $m^{-3}$) were applied as lower concentrations limit mass transfer rates, which would be applicable to the treatment of hydrophobic indoor air pollutants.

The focus was here on indoor air pollutants, as an example, but the approach to treat a mixture of hydrophobic contaminants using capillary bioreactors could also be applied to other scenarios, such as industrial emissions, gas upgrading, gas fermentation processes, or dilute-methane greenhouses gas (GHG) emissions as discussed elsewhere [14,23–26].

Indoor air quality (IAQ) is lacking the same focus as outdoor air pollution, while the health risks related to long-term poor IAQ have become more apparent [27]. The indoor air pollutants concentration is most of the time higher than the outdoor air pollutants concentration, especially in urban areas. Moreover, buildings are progressively being sealed against outdoor weather conditions to obtain heating and cooling energy cost savings [28–30]. Modern buildings increasingly rely on mechanical ventilation with reduced outdoor fresh air intake, leading to higher indoor air pollutant concentrations [31]. With humans spending about 90 % of their time indoors, effective simple indoor air purification methods are needed to obtain IAQ standards in addition to energy efficiency savings [31]. The types of indoor air pollutants and their current treatment methods are discussed elsewhere [31,32], as well as recent advances in biological methods for improving IAQ [33]. However, studies on synergistic algal-bacterial treatment of hydrophobic VOCs and $CO_2$ are rare, especially in a multi-channel capillary reactor. In an algal-bacterial bioreactor, microalgae can fix indoor $CO_2$ and $CO_2$ resulting from bacterial VOC mineralization, while producing oxygen during the photosynthetic process. This $O_2$ could be then utilized by heterotrophic bacteria mineralizing the VOCs. Thus, the capillary bioreactor was here explored as a potential platform to improve IAQ using synergistic algal-bacterial treatment of hydrophobic VOCs and $CO_2$.

## 2. Materials and methods

### 2.1. Chemicals

The liquid medium used in the capillary bioreactor experiments consisted of a Brunner mineral salt solution prepared as described elsewhere [13]. The silicone oil (polydimethylsiloxanes) that was used as second liquid phase exhibited a viscosity of 20 cSt (Sigma-Aldrich, Madrid, Spain). Silicone oil was chosen here because this NAPL fulfils critical selection criteria and is therefore commonly used as additional liquid phase in studies and applications that involves two-liquid phase bioreactors [15,16]. Criteria for the selection of a NAPL includes high affinity and high diffusivity for the target pollutants, high stability, and non-biodegradability (to avoid NAPL losses), low vapor pressure (to avoid NAPL losses due to evaporation), biocompatibility (non-toxic), non-hazardous nature (for operators and environment), and availability in bulk and at low cost. Silicone oil with a low viscosity was used in this study as the liquid viscosity can have an adverse effect on segmented flow regime in a capillary channel. This optimal flow regime for mass-transfer requires that the surface tension forces dominate over viscous forces [34], and because oil is more viscous than water and reduces the surface tension of water, it therefore tempers the capillarity of a liquid.

### 2.2. Liquid-gas flow pattern mapping

The different flow patterns of gas and liquid possible of flowing through a capillary channel are illustrated in Fig. 1. The occurrence of the optimal liquid-gas flow pattern for mass-transfer in a capillary channel was mapped at various gas-to-liquid flowrate ratios (G/L ratio), at various gas-liquid superficial velocities ($U_{G/L}$), and with and without the presence of a second liquid-phase (i.e., silicone oil). The parameters for predicting segmented flow in a single channel are well understood in clean liquids [35]. However, the presence of impurities such as a non-aqueous liquid-phase (e.g., silicone oil), and their effect on interfacial tension to maintain segmented flow are not well defined. The visual presence of the segmented flow regime was mapped in 1.5-meter--long capillary channels with different internal diameters ranging from 2.4 mm to 5.0 mm. The liquid flow and gas flow varied between 0 and 1.0 L $min^{-1}$. The gas consisted of ambient air and the liquid consisted of demineralized water or demineralized water containing 20 % (v/v) silicone oil (20 cSt). This abiotic experiment was undertaken with high silicone oil concentrations in a multi-channel configuration to better define experimental conditions in the multi-channel capillary bioreactor.

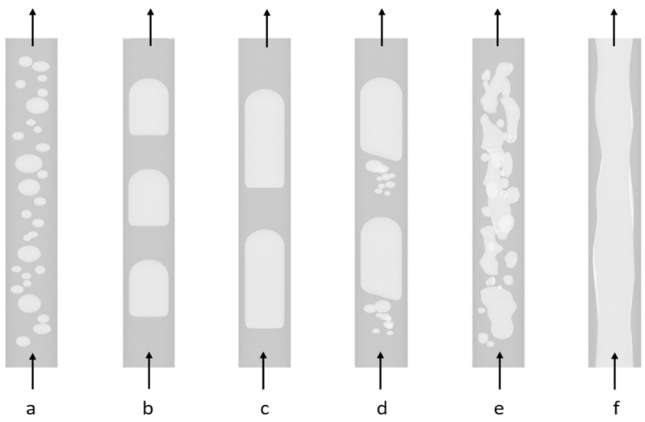



**Fig. 1.** Schematic of potential gas-liquid flow patterns in a capillary channel with (a) bubbly flow, (b, c) segmented flow/Taylor flow, (d) transition slug/churn flow, (e) churn flow, (f) falling film flow (adapted from Kreutzer and coworkers [34]).

### 2.3. Capillary bioreactor set-up

The main part of the capillary bioreactor consisted of 25 glass capillary conduits (internal diameter of 2.4 mm and external diameter 4.4 mm) with a length of 1.5 m each. Fig. 2 shows a schematic representation of the multi-channel capillary bioreactor. A pump (0.25 kW ESPA, Tecno-05–2 M) was used to recirculate the liquid (8.4 L) and a rotameter (Fisher & Porter, 10A1197A) was used to measure the liquid recirculation flow rate. A compressor (ABAC LT50) was used to introduce ambient air in the bottom reservoir via a perforated EPDM membrane. Inlet airflow and the air pressure at the inlet and outlet of the bioreactor were monitored by means of a rotameter (Aalborg, S/N 51588–2) and a pressure sensor (IFM, PN7097). Table 1 provides an overview of the main operating parameters during the 200 days of operation of the capillary bioreactor at an extremely low gas contact time of less than 1 second.

### 2.4. Impact of silicone oil on hydrophobic VOC removal in capillary bioreactor (stage I)

The capillary bioreactor was inoculated with biomass (initial concentration ≈ 0.5 g dry weight $L^{-1}$), which originally consisted of biomass from a chemostat fed with hexane, toluene, trichloroethylene and α-pinene, and fresh activated sludge from Valladolid (Spain) wastewater treatment plant. The biomass was taken from a previous study where its population structure was characterized by extracting and analysing the genomic DNA [13]. A VOC mixture was continuously injected to the inlet ambient air airstream using a syringe pump (Fisherbrand, Model 100). The VOC mixture contained α-pinene, hexane, and toluene as model compounds representing air pollutants, different in hydrophobicity and biodegradability.

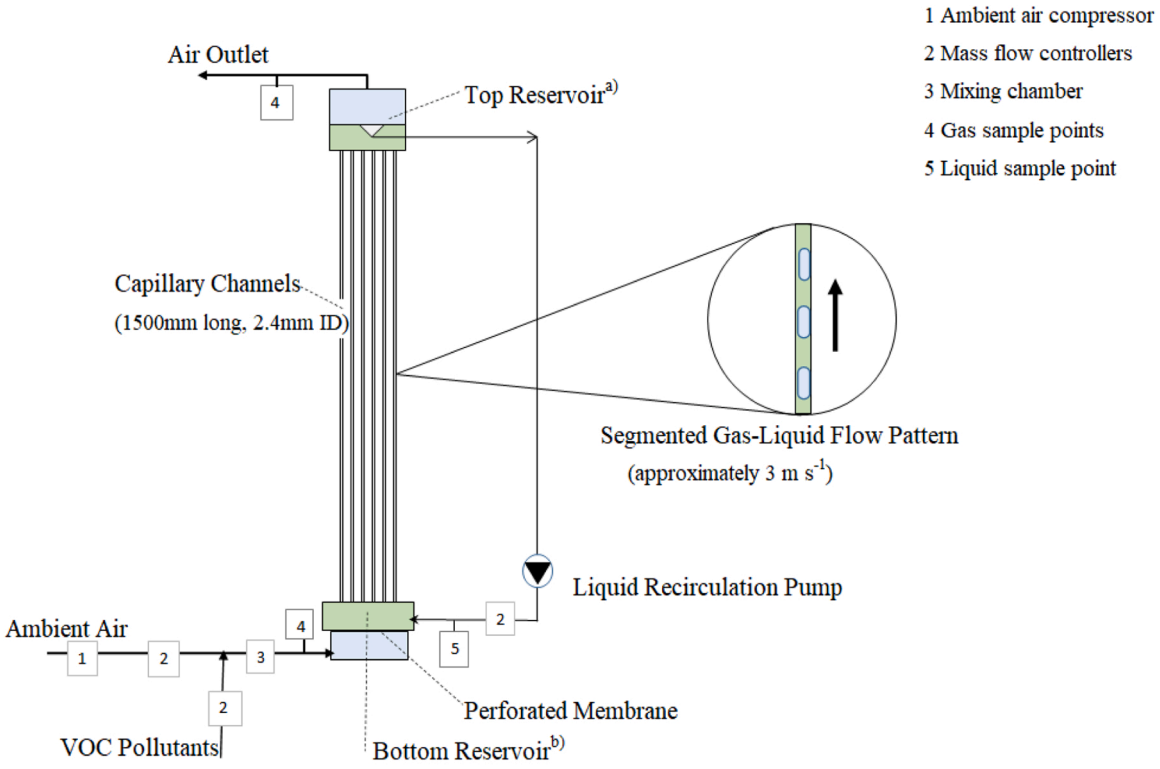
**Table 1**
Key operating conditions in the multi-channel capillary bioreactor.

| Stage /Gas Treatment | Days | Silicone Oil Addition (% v/v) | Recirculating Liquid Flow Rate (L $min^{-1}$) | Inlet Gas Flow Rate (L $min^{-1}$) | Empty Channel Residence Time (s) |
|---|---|---|---|---|---|
| **I** VOCs | 0–32 | 0 | 8 | 13.9 | 0.7 |
| | 33–95 | 5 | 8 | 13.9 | 0.7 |
| | 95–122 | 10 | 8 | 13.9 | 0.7 |
| | 122–150 | 10 | 6 | 13.9 | 0.7 |
| **II** VOCs + $CO_2$ | 150–200 | 10 | 6 | 13.9 | 0.7 |

The system was continuously operated at room temperature (controlled at 20 °C) while the liquid was recirculated in a closed loop and demineralized water was occasionally added to compensate for evaporative water losses or liquid losses due to liquid analyses. The applied gas and liquid flow rates of 13.9 L $min^{-1}$ and 8 L $min^{-1}$, respectively, resulted in an average empty channel gas residence time in the capillary channels of 0.7 s, where the empty channel residence time (ECRT) was defined as follows (Eq. 1):

$$ECRT = (V_c \times n_c) / (Q_g) \quad (1)$$

where $V_c$ is the internal volume of a capillary channel (L), $n_c$ the number of capillary channels in the capillary bioreactor (-), $Q_g$ the gas flow rate (L $s^{-1}$). The *ECRT* is similar to the empty bed residence time which is commonly used as a design parameter for gas treatment systems but does not represent the real contact time of the gas inside the capillary channel. The real contact time of the gas in the capillary channels would




a) The top reservoir (15 cm in diameter and 31 cm in height) served as gas-liquid disengagement zone.

b) The bottom reservoir (11 cm in diameter and 17.5 cm in height) served as gas-liquid mixing zone.

**Fig. 2.** Schematic representation of the experimental set-up of the capillary bioreactor.

be ~ 0.5 s as that would consider the liquid flow rate ($Q_L$) and the liquid film along the wall of the capillary channel, which can be expected to be in this study about 150 μm [36].

The recirculation liquid was not replaced by fresh medium during the entire experiment of 200 days. The following changes were performed for the first 150 days (Stage I): adding 5 % (v/v) silicone oil (with a viscosity of 20 cSt) on day 33 with a further increase to 10 % (v/v) on day 95; and a reduction of the liquid flow rate from 8 L $min^{-1}$ to 6 L $min^{-1}$ on day 122, while keeping the gas flow constant (see also Table 1). The biomass concentration, pH, and conductivity of the recirculation liquid were periodically determined. The inlet concentration of each VOC was similar, and all maintained between 2 and 5 mg $m^{-3}$ throughout the entire experiment (Stage I and Stage II), which are representative for highly concentrated indoor environments and some diluted industrial emissions.

### 2.5. Combined VOCs and carbon dioxide removal in capillary bioreactor (stage II)

The heterotrophic–phototrophic synergism between microalgae and bacteria in the capillary photobioreactor was investigated from day 150 onwards to elucidate whether it could be a sustainable platform for the biological removal of both $CO_2$ and VOCs in a single bioreactor. The capillary bioreactor was inoculated with a mixed microalgae consortium on day 150 (start of Stage II). During the final period of Stage I, the operating parameters remained unchanged to explore the potential of VOCs and $CO_2$ co-abatement. The microalgae biomass (300 mL with a concentration of 2.6 g dry weight $L^{-1}$ containing the main species *Pseudoanabaena sp*. (98 %) and *Chlorella vulgaris* (2 %) was obtained from a high-rate algal pond operated at the Institute of Sustainable Processes (University of Valladolid, Spain) increasing the overall biomass concentration in the capillary bioreactor by about 0.1 g dry weight $L^{-1}$. Additional illumination was provided with two cool white light emitting diodes (LEDs) strips (Mean Well, model LPV-100–12, 12 Volt, 8.5 Amp), which were wrapped around the bottom and top reservoirs, and the capillary channels. Aluminium foil was installed externally to direct the light towards the reactor surface. The average photosynthetic active radiation at the reactor wall was 100–150 μE $m^{-2}$ $s^{-1}$. The inlet ambient airstream contained an average $CO_2$ concentration of 412 ± 51 $ppm_v$, to which $CO_2$ produced from the mineralized VOCs in the bioreactor was added. The biomass concentration, pH, conductivity of the recirculation liquid, and the inlet/outlet $CO_2$ and VOC concentrations were also periodically measured during the Stage II duration of 50 days. The $CO_2$ removal during Stage II was defined as the difference in $CO_2$ concentration between the inlet and outlet airflow of the capillary reactor and considered the formation of $CO_2$ from the mineralized VOCs inside the capillary reactor.

### 2.6. Analytical procedures

The VOC concentrations in the inlet and outlet airstreams were measured once every weekday using Solid Phase Microextraction with an adsorption time of 10 minutes (SPME-fibre: CAR/PDMS 85 μm, Supelco) and a GC-FID (BRUKER-3900) according to the method described elsewhere [13]. The biomass concentration was determined according to Standard Method 2540 D. Samples for measuring $CO_2$ concentrations were drawn from the inlet and outlet of the capillary bioreactor during the illuminated period (Stage II) and analysed using a 430 GC-TCD (Bruker, Palo Alto, USA) equipped with a CP-Molsieve 5 Å (15 m × 0.53 mm × 15 μm) and a CP-PoraBOND Q (25 m × 0.53 mm × 10 μm) columns. The oven, injector and detector temperatures were maintained at 45, 150, and 200 °C, respectively. Helium was employed as the carrier gas at 13.7 mL $min^{-1}$.

### 2.7. Bacterial community structure

The community structure of the bacterial community inside the capillary bioreactor was characterized at the start of Stage I (day 1) and at the end of Stage II (day 200). The DNA was extracted from each biological replicate with a FastDNA™ SPIN Kit (MP Biomedicals, USA). PCR amplification of regions 16S-V4-V5 was performed by using the primers GTGCCAGCMGCCGCGGTAA, CCGTCAATTCCTTTGAGTTT connecting with barcodes. Libraries were checked with Qubit and real-time PCR for quantification, while a bioanalyzer was used for size distribution detection. Quantified libraries were pooled and sequenced on a paired-end Illumina platform to generate 250 bp paired-end raw reads in Novogene UK (Cambridge, UK). The whole process was performed through Python (V3.6.13) and adaptors were removed through cutadapt (V3.3). Paired-end reads were merged using FLASH (V1.2.11,http://ccb.jhu.edu/software/FLASH/). Data filtration and chimera removal were performed using the fastp (V0.23.1) software and the UCHIME Algorithm (http://www.drive5.com/usearch/manual/uchime_algo.html). Clustering of the sequences into Operational Taxonomic Units (OTUs) was as per the gene reference database SILVA (V138.1) and the ribosomal data base project (V18) [37] using QIIME (V 1.9.1). The sequences obtained have been deposited in Genbank as Bioproject PRJNA1020663. Bar graphs and heatmaps were plotted with R using the package ggplot2 [38] and R pheatmap [39]. Alpha diversity was calculated with QIIME (V 1.9.1) and displayed with R software (V 4.0.3). Function prediction according to marker genes was performed with the R package PICRUSt2 (V2.3.0) [40].

## 3. Results and discussion

### 3.1. Liquid-gas flow pattern mapping

This study established the optimal flow pattern to enhance the mass-transfer from the gas to the liquid phase (segmented flow with alternating liquid slugs and gas bubbles) (see Fig. 3), which was consistent with the observations from other capillary studies [8,25]. The presence of impurities such as a second liquid-phase (e.g., silicone oil), and their effect on interfacial tension, makes more difficult to predict the flow regime in a capillary channel. The addition of 20 % (v/v) silicone oil into water was here investigated to determine if segmented flow could be maintained at different gas and liquid flow rates. The addition of silicone oil poses a risk of disrupting proper segmented flow, as the oil reduces the surface tension of water, and, consequently, tempers the capillarity of a liquid. When oil is added to water, it disrupts surface tension because the strong hydrogen bonds between water molecules cannot be properly formed in the presence of oil. On the other hand, viscosity of a liquid slightly increases the capillarity of a liquid as per Eq. 2, when silicone oil is dispersed in the water as second liquid phase. Our results showed that the addition of silicone oil supported segmented flow at increased liquid velocities but not at increased gas velocities. Fig. 3 shows a map of the liquid flow and gas flow conditions supporting segmented flow with and without silicone oil in two channels different in diameter, which helped to define the experimental conditions in the multi-channel capillary bioreactor.

Kreutzer and co-workers [34] showed that a channel can have an internal diameter up to about 5 mm when using ambient air and water at room temperature to provide capillarity, meaning the dominance of surface tension forces over other external forces like gravity. Indeed, the occurrence of segmented flow could be obtained in our study in all capillaries up to 5 mm and was observed at gas velocities up to 0.5 L $min^{-1}$ and liquid velocities up to 0.5 L $min^{-1}$. At higher gas and liquid flow rate combinations, the segmented flow pattern could not be maintained in all capillary channels. This can be explained by the increase in the viscous drag forces relative to the surface tension forces, which compromises capillarity. The Capillary number (*Ca*) represents this relation between viscous drag forces and capillary forces (Eq. 2):

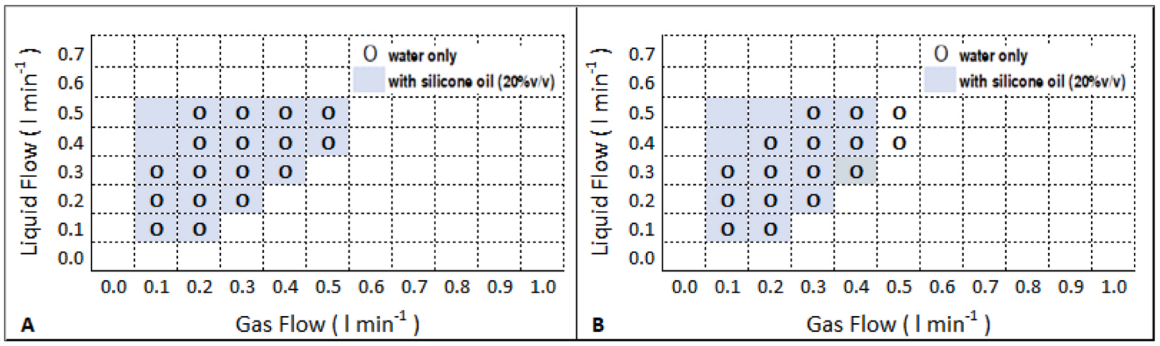



**Fig. 3.** Occurrence of segmented flow in capillary channel with internal diameter of 3.4 mm (A) and 5.0 mm (B) under the different gas flowrate and liquid flowrate conditions using water only and water with silicone oil.

$$Ca = \mu\, v / \gamma \quad (2)$$

where $\mu$ is the viscosity (Pa $s^{-1}$), $v$ the liquid velocity (m $s^{-1}$), $\gamma$ the surface tension of the liquid in the gas phase (N $m^{-1}$). Higher liquid velocities will result in a higher capillary number, which becomes less dominated by capillary forces such as surface tension and explains why segmented flow can only be obtained up to a certain liquid velocity.

### 3.2. Impact of silicone oil on hydrophobic VOC removal in a capillary bioreactor (stage I)

The removal of the hydrophobic VOCs was investigated in the capillary bioreactor with and without silicone oil as non-aqueous phase liquid under the segmented flow pattern conditions. The VOC removal after the initial start-up period (15 days) in the capillary bioreactor without any silicone oil addition was on average 45 ± 6 % for α-pinene, 44 ± 10 % for hexane and 81 ± 3 % for toluene (Fig. 4), which is consistent with a previous study undertaken in a similar bioreactor configuration [13].

The addition of 5 % (v/v) silicone oil on day 33 did significantly increase the removal efficiency (RE) of α-pinene from 45 ± 6 % to 95 ± 3 %. An instant peak in α-pinene RE was observed directly after the addition of the oil, due to the initial absorption in the silicone oil, then increasing to remain stable after two days. An increase to 10 % (v/v) silicone oil on day 95 further enhanced the RE of α-pinene to 98 ± 2 %. This is remarkable since the addition of silicone oil did not have any significant effect on the removal of hexane regardless of the concentration (5 or 10 % v/v). Both α-pinene and hexane have a high affinity for silicone oil as reflected by the gas-oil partitioning coefficient ($H_{G/Silicone\ Oil}$) when compared to the gas-water partitioning coefficient ($H_{G/Water}$) as illustrated in Table 2.

The addition of 5 % (v/v) silicone oil (on day 33) did not initially increase the RE of toluene but resulted in a steady increase of toluene removal from about 80 % (81 ± 3 %) to just above 90 % (93 ± 2 %) by day 40, which likely indicated microbial adaptation to the new condition with the dispersed second liquid phase. A further increase to 10 % (v/v) silicone oil on day 95 did not show any further enhancement of the toluene removal, and in fact, slightly reduced the RE of toluene to 86 ± 2 %. Of the VOCs evaluated, toluene has the lowest dimensionless Henry-coefficient ($H_{g/Water} = 0.3$; Table 2) and was removed better than hexane and α-pinene during the initial period without silicone oil, confirming that $H_{g/Water}$ is a key factor for gas-liquid mass transfer and associated RE in a capillary bioreactor.

The initial α-pinene RE was slightly lower compared to that of hexane (Fig. 4) and is unlikely to be the result of mass-transfer limitations. This is because hexane has a much higher dimensionless Henry-coefficient ($H_{G/Water}$) than pinene (71 *vs* 8 as illustrated in Table 2), meaning α-pinene is significantly better absorbed from the gas phase into the water phase at equal gas concentration. The pinene gas concentration was also on average slightly higher than the hexane concentration during the entire experiment (4.7 mg $m^{-3}$ vs 2.2 mg $m^{-3}$), and a higher concentration benefits mass transfer. Moreover, α-pinene has a higher octanol-water partitioning coefficient (log $K_{o/w} = 4.83$) compared to hexane (log $K_{o/w} = 3.90$). The octanol-water partition coefficient (log $K_{o/w}$) is typically used to quantify the hydrophobicity of a pollutant and may be used to predict the uptake of a compound into biological membranes. $K_{o/w}$ is the most common way to express lipophilicity of a compound and has been shown to influence the removal efficiency of VOCs in conventional biological gas treatment systems [41].

The findings in this study suggest that the initial α-pinene removal was limited by biokinetics as the α-pinene may be more difficult to degrade due to its higher molecular weight and its different (bicyclic) structure. The biodegradation of α-pinene could require partial enzymatic conversion into smaller molecules in the liquid phase before they can be taken up by the bacterial cells more readily [44]. The addition of silicone oil may have provided a buffer for the α-pinene and/or its metabolites, thus mitigating previous biokinetic inhibition. The steep improvement of α-pinene RE after silicone oil addition in the capillary bioreactor from 45 ± 6 % to 95 ± 3 % is consistent with observations in a study that involved a conventional biotrickling filter where the α-pinene RE improved from 50 % to 98 % after the addition of 5 % (v/v) silicone oil [45]. However, an important difference between both experimental studies is the empty bed gas contact time, which is more than one order-of-magnitude shorter in the capillary bioreactor (0.7 seconds in this study *vs* 14 seconds in the conventional biotrickling filter study), while requiring theoretically the same order-of-magnitude of energy per volume of treated air.

Similarly, the removal of hexane in this study might also have been hampered by biokinetic limitations rather than mass transfer, which was already boosted by the internal recirculation in the segmented flow pattern inside the capillary channels. Hexane RE did not increase with the additions of the NAPL, even though the affinity of silicone oil for hexane is more than 12,000 times higher than for water. Muñoz and co-workers [46] also observed that the addition of silicone oil did not increase hexane removal in their stirred bioreactor tank study and identified that the formation of metabolites would have been the most likely reason for the inhibition. This would also be consistent with the study by Li et al., [19], who detected the hexane degradation intermediates 2-hexanone, 2-hexanol, 1-butanol, acetic acid, and acetone in the aqueous phase in stirred bioreactors with silicone oils treating hexane. Moreover, Cantera and co-workers [47], observed improved methane abatement in a stirred bioreactor with silicone oil as NAPL after increasing dilution rate of the aqueous phase. It was therefore concluded that the deliberate absence of replenishment of the recirculation liquid in our study may also have contributed to metabolic inhibition of hexane.

A further increase in α-pinene removal was obtained when the liquid

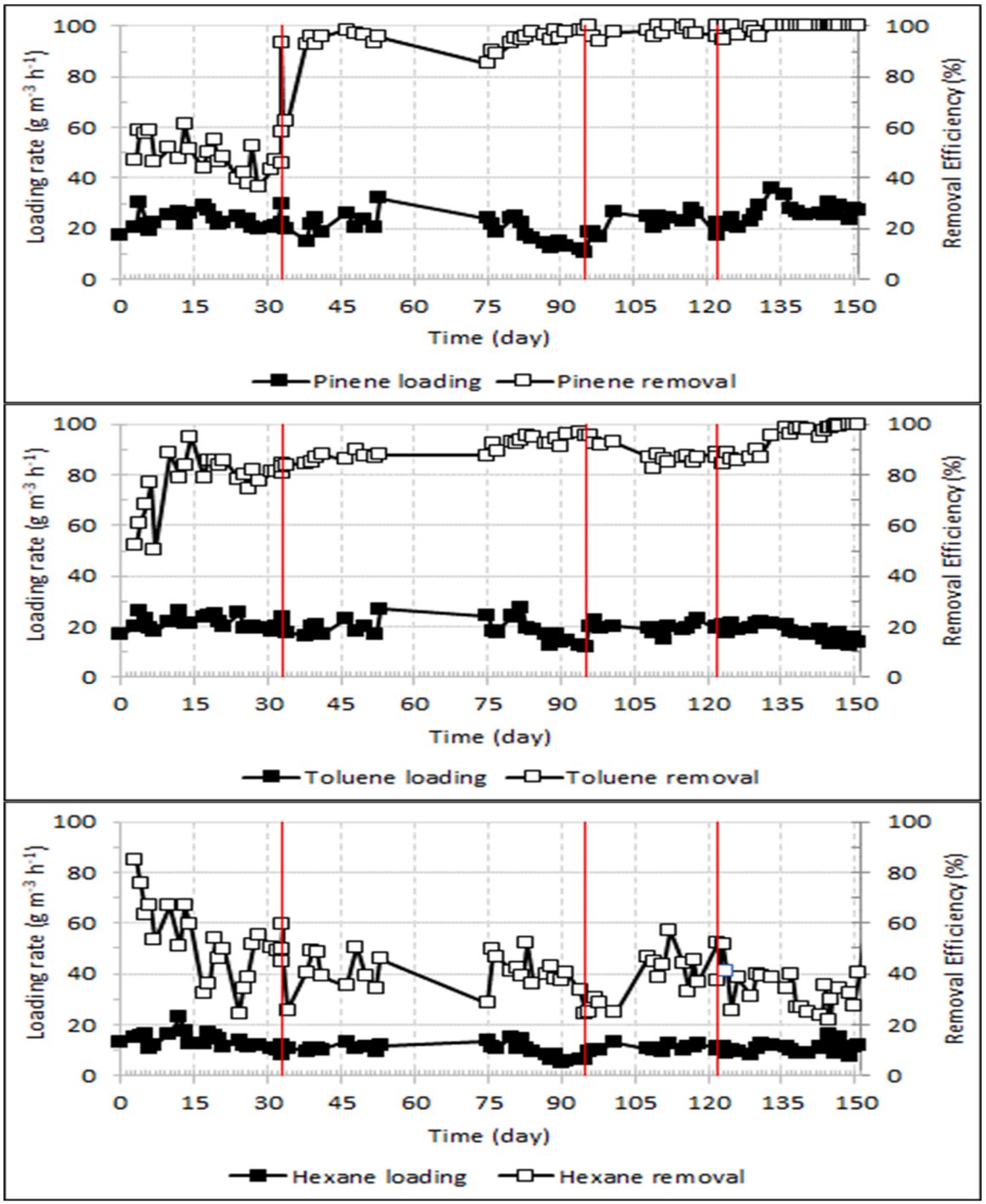



**Fig. 4.** Time course of the loading rates (■) and removal efficiencies (□) of α-pinene (upper), toluene (middle) and hexane (lower) in the capillary bioreactor during Stage I (day 0 – 150), with the vertical lines indicating the days at which key operating changes were introduced: addition of 5 % (v/v/) silicone oil (day 33), increased to 10 % (v/v) silicone oil (day 95), and increase gas-to-liquid ratio (day 122).

flow was changed from 8 to 6 L $min^{-1}$ on day 122, increasing the Gas-to-Liquid ratio, while keeping the gas flow rate constant. The RE of α-pinene increased from 98 ± 2 % to 99.5 ± 1 %. Similarly, an increase was observed in the average removal of toluene, which increased from 86 ± 2 % before day 122–95 % ± 5 % after day 122, reaching over 98 % removal. This may be explained by further microbial adaptation or general hydrodynamic stability of the bioreactor system, such as a more homogeneous gas bubble-liquid slug length distribution among the twenty-five capillary channels. The increase in RE of both pinene and toluene occurred despite the slightly lower overall mass-transfer coefficient ($K_La$) of the capillary bioreactor system at a reduced superficial velocity (of the gas bubble-liquid slug) as determined in a previous study [13]. The removal of hexane, on the other hand, did not increase but rather slightly decreased from 44 ± 7 % to 33 ± 6 %, which may be explained by further metabolite accumulation due to the absence of replenishment of the bioreactor liquid phase.

The results show that the operation and performance of the capillary bioreactor were stable without replacing the liquid in the reactor: steady VOC removal performance without foam formation while maintaining segmented flow in all capillary channels. In addition, the pH remained

**Table 2**
Water Solubility and Partitioning Coefficients of Target Gaseous Compounds[a].

| Compound | Molar Mass[b] | Water Solubility[c] | $H_{Gas/Water}$ | log $K_{Octanol/Water}$ | $H_{Gas/Silicone\ Oil}$[d] |
|---|---|---|---|---|---|
| α-Pinene ($C_{10}H_{16}$) | 136.2 | 2.5 | 8 | 4.83 | 0.00018 |
| Hexane ($C_6H_{14}$) | 86.2 | 9.3 | 71 | 3.90 | 0.0058/ 0.0044 |
| Toluene ($C_7H_8$) | 92.1 | 526 | 0.3 | 2.73 | 0.00064/ 0.00089 |
| Carbon dioxide ($CO_2$) | 44.0 | 2900 | 1.2 | 0.83 | 0.15 |
| Oxygen ($O_2$) | 32.0 | 39 | 32 | 0.65 | 3.6 |

[a] at 25 °C [16,42,43]
[b] g $mol^{-1}$
[c] mg $L^{-1}$
[d] 20 cSt silicone oil

around 7.5 during the 150 days of the experiment (Stage I), which suggested that no acidic or alkaline degradation products were accumulated at substantial concentrations.

The removal efficiencies of the VOCs observed in the capillary bioreactor were very high considering that the inlet VOC concentrations were relatively low (< 5 mg $m^{-3}$, with mass transfer proportional to gas concentration) and that the gas contact time was extremely low (~ 0.7 seconds). Conventional biological gas treatment systems typically require an empty bed residence time that is between one and two orders of magnitude higher for the abatement of hydrophobic compounds [2,48,49].

While the gas-liquid mass-transfer is intensified using segmented flow inside the capillaries, most of the biodegradation occurs within the reservoirs as they hold most of the liquid containing the biomass. This would be like a conventional bioscrubber that has liquid recirculating between two reactor units. In the first reactor-unit, the gas contactor, compounds are absorbed from the gas-phase in the liquid phase, and in the second unit the compounds are further converted by microorganisms suspended in the liquid (suspended growth biomass). The average VOC removal rate in the gas contactor was 43 ± 8 g VOC $m^{-3}$ $h^{-1}$ during Stage I and dropped to 35 ± 9 g VOC $m^{-3}$ $h^{-1}$ during Stage II. Similarly, the average biological degradation rate in the recirculating liquid was 0.9 ± 0.2 mg $L^{-1}$ $h^{-1}$ during Stage I and 0.7 ± 0.2 mg $L^{-1}$ $h^{-1}$ during Stage II.

### 3.3. Combined VOCs and $CO_2$ removal for IAQ enhancement (stage II)

Instant lower carbon dioxide concentrations were observed after the introduction of the microalgae to the capillary photobioreactor (Fig. 5). This confirms a net $CO_2$ consumption despite the $CO_2$ produced from VOC mineralization by the bacteria achieving complete carbon sequestration from the removed VOCs. During the following 50 days, the outlet $CO_2$ concentration of the bioreactor remained in the range of 10 ± 5 % lower than the inlet $CO_2$ concentration while observing a slow natural increase of the pH mediated by photosynthesis. The pH increased over a period of 30 days, from about 7.3–9.4, while $CO_2$ removal remained at 10.4 ± 4.8 % until day 200, when the experiment was stopped. The increase in the pH of the cultivation broth can be explained by photosynthetic activity in the absence of replenishment of the bioreactor liquid in this study. Algae remove $CO_2$ from the recirculating liquid, reducing its alkalinity, which can subsequently raise the pH of the liquid.

A net $CO_2$ consumption was observed during the entire Stage II achieving complete carbon sequestration from the removed VOCs. VOC removal during the initial phase of Stage II was similar to that during the final period of Stage I, but then changed, likely due to the pH slowly increasing from 7.3–9.4 over the course of 50 days (from day 150 to day 200). The RE of α-pinene decreased from 99.5 % to about 75 % on day 158 when the increasing pH was around 8.0 (data not shown). The RE of toluene decreased from 95 % on day 185 to about 70 % when the pH reached ~ 9.3. During the same period, the RE of hexane increased from ~ 30–55 % (data not shown). While both the RE of α-pinene and toluene decreased due to microbial inhibition at the high pH, the RE of hexane increased likely due to enzymatic changes within the microbial community removing toluene, as the changes in the removal performance occurred at the same time (around day 185).

The potential of algal-bacterial symbiosis for the combined abatement of $CO_2$ and VOCs has not been studied abundantly [50], and especially not in relation to IAQ. Nonetheless, the technical feasibility of the combined VOCs and $CO_2$ consumption by a mixed microbial consortium of microalgae and bacteria in the capillary photobioreactor discussed herein agrees with observations of algae-bacterial treatment systems by other authors [1,50,51,52]. It is unlikely that there is severe competition between microalgae and bacteria. The bacteria dominating the bioreactor both are heterotrophic, so there is no competition for $CO_2$, and some microalgae can bio transform VOCs, but at a rate likely lower compared to the bacteria biotransformation rate of VOCs in our study. In algal-bacterial bioreactors, microalgae produce oxygen in the presence of light, and bacteria utilize the oxygen to oxidize the VOCs. The $CO_2$ produced as a by-product from aerobic VOCs degradation is concomitantly fixed by microalgae. On average, up to 24.8 % of the $CO_2$ removed in the bioreactor is produced in-situ from VOC mineralization, while the rest of the $CO_2$ removed in the capillary bioreactor (at least 75.2 %) comes from the inlet ambient air. Indeed, there is a net $CO_2$ consumption despite the $CO_2$ produced during VOC mineralization, achieving complete carbon sequestration from the removed VOCs along with additional $CO_2$ removed from the inlet ambient air.

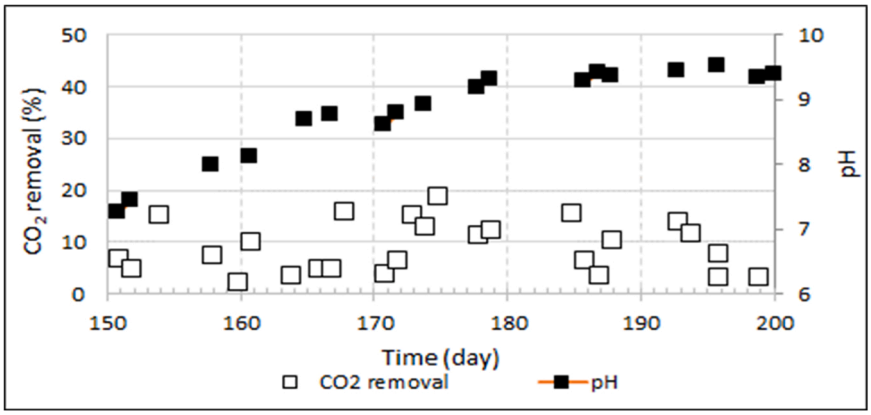



**Fig. 5.** Time course of the removal efficiencies (□) of $CO_2$ and the pH (■) in the capillary photobioreactor during Stage II (day 150 – 200).

The reduction of the inlet $CO_2$ concentration was about 10 % (Fig. 5), corresponding to a removal of 40 $ppm_v$ between the inlet and the outlet $CO_2$ concentration in a single pass (less than 1 second) of the gas through the capillary bioreactor while treating VOCs. Thus, when the airflow is recycled, in a similar fashion to the recycling of ventilation air of an occupied room, this would still present a continuous removal of $CO_2$ from the room. The aim is not to achieve near-complete $CO_2$ removal is a single pass of the gas through the system, unlike end-of-pipe treatment technologies for industry emissions. The implementation of capillary photobioreactors to improve IAQ of occupied rooms could minimize or almost eliminate ambient air intake and significantly reduce the energy costs for heating and/or cooling typically required for conditioning outdoor air intakes. When a $CO_2$ RE of 10 % is applied to a typical baseline ventilation rate of three air volume changes per hour in an occupied room, a constant $CO_2$ concentration can be maintained when the $CO_2$ production does not exceed a rate of 100 $ppm_v$ $CO_2$ per hour. A higher $CO_2$ production rate would be feasible if the $CO_2$ concentration remains below 1000 $ppm_v$, which is considered a safe value with no adverse effects on human health and well-being. This threshold is also the maximum limit in most green building certification schemes [53,54]. Alternatively, higher ventilation rates would be necessary to increase the overall $CO_2$ elimination capacity to maintain the required IAQ at a reduced outdoor air intake. The reduction in outdoor air intake while maintaining low enough levels of pollutants in a room when an indoor air purifying system is employed is called the clean air delivery rate (*CADR*) of that system [55]. In summary, the overall purification capacity per volume of indoor space is a better performance criterium for indoor air purification systems than the single pass purification

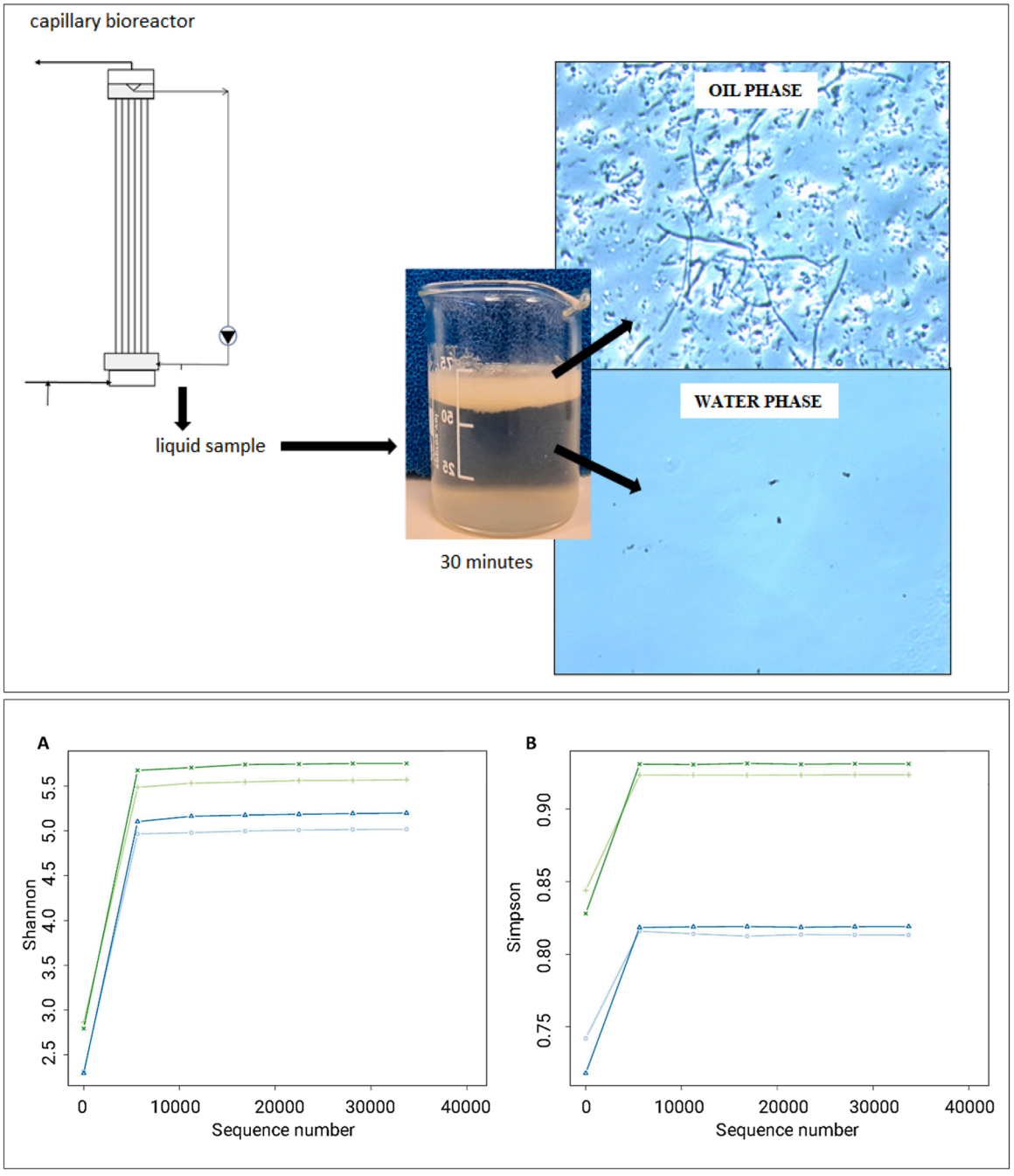



**Fig. 6.** Above photos of the microbial appearance in the recirculation liquid of the capillary bioreactor at the end of Stage I after separating the two-liquid Stages. Below the Shannon (A) and Simpson (B) alpha diversity indexes at the start of Stage I (blue) and at the end of Stage II (green) both conducted in duplicate.

efficiency.

Maintaining low $CO_2$ levels in occupied spaces, in addition to maintaining low VOCs levels, is important as multiple studies have shown that human performance and wellbeing is directly negatively influenced by high $CO_2$ concentrations [56,57]. This involves workplace productivity, the quality of sleep alongside the next day performance and other negative symptoms like drowsiness, panting, and short breath. Moreover, when ambient outside air supply is maintained at the minimum ventilation rates per current professional standards such as ASHREA, generously occupied spaces can still result in $CO_2$ concentrations higher than the safe value of 1000 $ppm_v$ [56].

Biological approaches for improving IAQ are promising, but only when they can properly address the bioavailability of low concentrations of hydrophobic pollutants, provide $CO_2$-removal as well as guarantee microbial safety. A capillary bioreactor may provide an opportunity to improve IAQ via the co-abatement of VOCs and $CO_2$. Combining it with ultraviolet (UV) photolysis for the elimination of bioaerosols can further polish the biologically purified air, as reviewed elsewhere [24].

### 3.4. Microbial characterization

Liquid samples from the capillary reactor were taken at the beginning of Stage I and at the end of Stage II to analyse the microbial community. Microscopic investigations during Stage I revealed that nearly all the biomass resides inside or adhered to the silicone oil phase rather than in the water phase (see upper photos of Fig. 6). No biomass attached to any of the glass capillary channels was observed for the 150-days operation of the capillary bioreactor. This indicated that the main bacterial activity occurred nearly exclusively inside the silicone oil phase and/or adhered to the silicone oil-water interphase. The liquid-phase specific biocatalytic activity in the aqueous phase and the oil phase was not quantified in this study. The presence of micro-water droplets inside the silicone oil cannot be ruled out especially under the highly turbulent operating conditions inside the capillary channels. The finding was similar to the observation done by Muñoz and co-workers [46] and Hernandez and co-workers [58], who confirmed the activity of a hydrophobic microbial consortium inside and/or at the NAPL (silicone oil) when treating high concentrations of hexane in a continuously stirred bioreactor. They observed the highest enhancements in VOC elimination capacity when microbial cells were confined inside and/or adhered at the NAPL, which may also explain the superior elimination efficiencies obtained in our study. Microbial population changes over time in the capillary bioreactor have been confirmed in this study and changes in microbial cell hydrophobicity induced by the presence of silicone oil could also have played an important role for the biomass to adhere at the silicone oil phase rather than reside in the water phase.

No accumulation of biomass on the walls of the capillary glass channels was observed for the 150-days operation of the multi-channel capillary bioreactor during Stage I. This observation is consistent with the findings in other studies where no biofilm formation was observed inside capillaries [13,14] due to the relatively high shear forces. The prevention of biofilm formation was systematically studied by Studer [59], who showed that bacterial biofilm accumulation could be simply prevented with relatively low shear forces, which confirms the observations in the study discussed herein. Nevertheless, the experiment was stopped by day 200 because of the clogging of three capillary channels mediated by the increase in algal biomass concentration during Stage II. The Stage II operation of the capillary bioreactor identified that operational adjustments would be required as microalgae, unlike bacteria in Stage I, seem capable of building a biofilm despite the relatively high shear-forces in the channels. These operational adjustments could involve placing the capillary channels in the dark and applying light only to the liquid recirculation reservoir or regular cleaning of the capillary channels. In addition, this study showed that pH-neutralization (and/or replenishment of the recirculation liquid) would be required to maintain a stable pH during co-abatement of VOCs and $CO_2$.

Metagenomic amplicon sequencing revealed that the bioreactor presented a more specialized and less diverse community at the start of Stage I, while bacterial richness and evenness significantly increased during the study (ANOVA $< 0.05$) (see Supplementary Material). The community at the start of Stage I relied only on the recalcitrant VOCs treated (α-pinene, toluene, and n-hexane), while the addition of silicone oil and/or microalgae seems to have enhanced bacterial growth, diversity, and carbon co-metabolism potentially due to the algal characteristic release of dissolved organic compounds and phytohormones to the phycosphere [60] (see Supplementary Material). The variance between the bacterial genera found (per taxon) in each sample shows the great difference between the dominant bacterial communities at the start of Stage I and the end of Stage II (see Figure S1 of the Supplementary Material).

The enrichment under the treated VOCs at the start of Stage I favoured the growth of a specialized community shaped by members of the uncultured OLB8 cluster from the family *Saprospiraceae* (42.1 % ± 0.1 %) (genera abundance clustering bar plot in Supplementary Material). *Candidatus* genera from the family *Saprospiraceae* are known to be highly abundant in biological wastewater treatment processes. Recent shotgun genomic studies have confirmed that they have the capability of degrading complex and recalcitrant organic molecules [61], thus they were most likely involved in the catabolism of the target VOCs in Stage I. Other bacterial representative genera were members of the genus *Methylibium* (7.4 % ± 0.5 %) and *Donkdonella* (2.2 % ± 0.6 %). In contrast, these genera had almost negligible representation at the end of Stage II. Stage II was dominated by uncultured members of the family *Blastocatellaceae* (21.3 % ± 0.01 %). Microalgae (detected throughout chloroplast identification) and the cyanobacteria *Nodosilinea* were also representative in Stage II (17.3 % ± 0.2 % and 7.5 % ± 0.01 %) (see Supplementary Material). Interestingly, bacteria previously related to α-pinene, toluene and n-hexane metabolism, such as the genera *Hydrogenophaga* (2.8 % ± 0.4 %), *Pseudofulvimonas* (1.0 % ± 0.01 %) and *Pseudomonas* (0.7 % ± 0.02 %) were detected in Stage II, but at low relative abundances [62]. This fact confirmed that the main metabolisms of Stage I were related to VOC removal, while in Stage II photosynthesis and chemoorganotrophy of the generated metabolites were most probably the prevalent metabolisms.

The bacterial diversities at the start and at the end of the experiment were determined and enhanced significantly during the 200-day operation of the capillary bioreactor. The Shannon and Simpson alpha diversity indexes increased from 5.1 to 5.6 and from 0.82 to 0.94, respectively (see diversity indexes in Fig. 6). The bacterial diversity has been identified as an indicator of community stability and functional resilience towards perturbation [63] and could be an explanation of the stable performance during the 200-day operation of the capillary bioreactor.

## 4. Conclusions

Toluene, α-pinene and hexane removals up to 99, 98, and 55 %, respectively, were achieved in the multi-channel capillary bioreactor with 10 % (v/v) silicone oil dispersed in the recirculating liquid operated at a gas contact time lower than 1 second. The addition of silicone oil increased the RE of α-pinene from 45 ± 6 % to 98 ± 2 % over two days, likely due to the silicone oil alleviating biokinetic inhibition by acting as a buffer for the VOCs and their metabolites. For toluene, the RE gradually increased after silicone oil addition from 81 ± 3 % to 99 ± 1 % over eight weeks, likely due to microbial adaptation. The RE of hexane did not increase after silicone oil addition, potentially due to inhibition of hexane or its metabolites as the bioreactor was deliberately operated without replenishment of the recirculation liquid.

Interestingly, the biomass adhered to the silicone oil phase rather than residing in the water phase. In addition, bacterial diversity was

substantially enhanced over the 200-day operation, likely contributing to the stable performance of the capillary bioreactor. Long-term operational requirements identified for the capillary bioreactor include pH-neutralization and/or replenishment of the recirculation liquid, especially during co-abatement of VOCs and $CO_2$.

An instant reduction of the outlet $CO_2$ concentration compared to the inlet $CO_2$ concentration was observed after introducing the microalgae into the capillary bioreactor. A slow natural increase of the pH caused by photosynthesis was recorded confirming photosynthetic activity. Net $CO_2$ consumption was observed, with complete carbon sequestration from the removed VOCs and additional $CO_2$ removal from the inlet ambient air. This confirms the potential of capillary bioreactors as a platform for the co-abatement of $CO_2$ and hydrophobic VOCs.

This work revealed that a capillary bioreactor may be an innovative gas treatment technology and could open new opportunities for the abatement or purification of industrial gases containing hydrophobic VOCs, as well as new opportunities for improving the indoor air quality of occupied rooms through the removal of VOCs and $CO_2$.

## CRediT authorship contribution statement

**Norbertus J R Kraakman:** Writing – original draft, Methodology, Investigation, Conceptualization. **Javier Gonzalez-Martin:** Visualization, Validation. **Cora Sanchez-Gracia:** Investigation. **Sara Cantera:** Writing – original draft. **Raquel Lebrero:** Writing – review & editing, Supervision. **Raul Munoz:** 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.

## Data availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.113695.

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