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Hydrophobic air pollutants removal at one second gas contact in a multi-channel capillary bioreactor

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ABSTRACT

Biological processes are increasingly applied for gas purification as a sustainable and economical alternative to conventional physical-chemical processes (chemical absorption, incineration, adsorption). Although biological gas treatment is accepted as an economical, safe, and reliable air pollution control technology, it faces important limitations when applied for the treatment of poorly water-soluble compounds due to mass transfer limitations. A twenty-five capillary channels bioreactor was studied to characterize mass transfer coefficients and the removal of hydrophobic air pollutants under segmented gas-liquid flow pattern. The removal efficiency of hexane, toluene and α-pinene vapors reached values up to about 75%, 99% and 75%, respectively, at a gas contact time of less than 1 s, which is at least one, but closer to two orders of magnitude shorter than conventional biological gas purification systems. The bioreactor displayed stable operation for 100 days and was robust against common upsets, which opens the new opportunities for expanding the application field of biological processes for air pollution control and the mitigation of greenhouse gases in dilute air streams.

Synopsis: This study breaks through existing barriers of gas treating biotechnologies which allows expansion of the application field of more sustainable processes for air pollution control.

1. Introduction

The economic cost and social impact of air pollution are high worldwide. For example, the yearly costs illnesses and premature deaths attributed to air pollution for the European Region alone was estimated to be US$ 1.575 trillion [49]. Pollution prevention should always be considered first, but cannot always be applied in a cost-effective or technically feasible manner. Thus, effective abatement technologies to eliminate air pollutant emissions from industrial processes or to avoid the build-up of air pollutants in occupied spaces are needed. Bioprocesses for air pollution control have gained acceptance over the last several decades as they have shown in many applications to be sustainable and cost-effective alternatives to conventional physical or chemical technologies for treating gaseous streams [10,19,46,48].

Nevertheless, current biological air pollution control techniques are hampered by their relative inability to treat hydrophobic pollutants [11,13,24]. This currently limits their optimization in existing fields such as industrial waste gas treatment, since biological techniques require significantly larger reactor systems compared to their physical-chemical counterparts (i.e., biological techniques currently require gas contact times typically between 25 and 60 s for effectively removing hydrophobic pollutants, while physical and chemical treatment systems such as chemical scrubbing and activated carbon adsorption requiring typically between 2 and 4 s depending on the application). An emerging application is the biological treatment of dilute off-gases containing methane, a potent greenhouse gas (GHG) [33], which is feasible but requires even larger gas contact times [28].

In addition, the relative inability of biological systems to treat hydrophobic pollutants limits their application in new fields such as indoor air quality control [15,16,25,35]. Buildings such as offices, hotels, and shopping malls are more and more sealed to achieve heating and cooling energy cost savings and they are increasingly relying on mechanical ventilation with reduced fresh ambient air ingress [9,12]. Nature-based solutions to purify indoor air could provide multiple benefits including

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pollution control and delivering additional social-economic benefits such as aesthetics and improved human well-being [25,38,46].

Biological processes for gas treatment typically operate under mass transfer limited conditions when treating hydrophobic pollutants. Mass-transfer rates may be enhanced by increasing the specific gas-liquid-biofilm contact area in laminar contactors (e.g., biofilters or bio-trickling filters) or by increased mixing in turbulent contactors (e.g., stirred tank bioreactors or airlift bioreactors), all requiring an increase in power consumption due to increased pressure losses or increased mixing intensity, respectively [26]. Laminar flow refers to a flow regime where gas or liquid flows in parallel layers with minimum disturbance, and where mass transfer is dominated by diffusion. Because diffusion through liquid is relatively slow compared to diffusion through gas, mass transfer enhancement in liquid can be obtained through the motion of the fluid also called advection (e.g., mixing). Capillary reactors with a specific gas-liquid flow pattern (segmented flow pattern) can create internal liquid circulation that has shown to enhance the mass transfer between the gas and liquid phases. Moreover, in a capillary reactor the capillary forces are dominant over other forces as such gravity and viscosity facilitating a low pressure drop over the channels resulting in minimum energy requirements [18,26,30,41]. In recent years, there has been increasing interest in capillary microreactor technology for process intensification, in multiple applications from emulsion production, synthesis of fine chemicals, and more recently in environmental remediation [41]. Capillary gas-liquid bioreactors are promising for environmental applications as was shown in previous studies [6,8,17,26,31,32,42]. Nevertheless, these studies on capillary gas-liquid bioreactors are limited, mostly dealing with short single capillary channels, limitation test duration or limited in operating conditions and not focused on treating hydrophobic gaseous compounds.

In this study, the fundamental understanding of (1) a multi-capillary channel gas-liquid bioreactor and (2) the removal mechanisms of three model hydrophobic gaseous pollutants were studied in a capillary bioreactor at extremely low gas contact times. Abiotic and biotic experiments were performed to map the gas-liquid flow patterns at different gas and liquid velocities, followed by the determination of the mass transfer coefficient (K_La) under multi-channel segmented flow conditions. Finally, the performance of a multi-channel capillary bioreactor was studied for the continuous elimination of three model hydrophobic air pollutants and tested for operational stability over a 100-day period, while the dynamics of microbial population structure was monitored.

2. Material and methods

2.1. Capillary reactor set-up

The capillary bioreactor was built of 25 glass capillary tubes with an internal diameter of 2.4 mm, 1 mm wall thickness, and a length of 1.5 m. The liquid phase was recirculated using a pump (0.25 kW ESPA Tecno-05–2 M) and measured with a rotameter (Fisher&Porter 10A1197A). The total liquid volume in the bioreactor was 8.4 liter (L). Ambient air from a compressor (ABAC LT50) was introduced in the bottom reservoir via a 3 mm thick perforated PDMS membrane containing about 400 needle holes with a diameter of 0.4 mm. The airflow and the pressure were measured with a rotameter (Aalborg, S/N 51588–2) and a pressure sensor (IFM PN7097), respectively. A schematic representation of the set-up is shown in Supplementary Fig. S1.

2.2. Pressure loss

Prior to selecting the internal diameter of the capillary channel for the capillary bioreactor, the pressure required for passing ambient air through different capillary channels was determined at different gas velocities. Three glass channels diameters (AFORA; T64, T65 and T67) were used with an internal diameter of 2.4, 3.4 and 5.0 mm, respectively, all 1.5 m in length. The airflow was measured using a rotameter and the pressure drop was determined using a U-shaped water gauge. The measured pressure losses were converted into Pascal per meter of capillary channel.

2.3. Liquid-gas flow mapping

Different liquid-gas flow patterns can be obtained in a capillary channel (see Supplementary Fig. S2). The gas-liquid flow pattern for optimal mass-transfer is the segmented flow pattern, also called bubble train flow or Taylor flow, characterized by alternating gas bubbles and liquid slugs with lengths greater than the capillary diameter [27,30]. In this flow regime, the internal liquid circulation increases the gas-liquid mass transfer through local mixing without affecting the axial dispersion [30]. The establishment of the segmented flow regime was determined visually by varying the gas to liquid flowrate ratio (G/L ratio) and the gas-liquid superficial velocities ($U_{G/L}$), with the gas and liquid flows varied between 1.4 and 23.5 L min^{-1} and 1–14 L min^{-1}, respectively. Successful segmented flow was considered when the flow pattern could be established along the entire capillary channel length and in all 25 channels. The gas and liquid consisted of ambient air and demineralized water containing 0.3 M Na_2SO_4, while the segmented flow was also mapped with liquid containing biomass (0.25, 0.5 or 1.0 g dry weight L^{-1}).

2.4. Mass transfer coefficients

The mass transfer rate for oxygen from the gas phase to the liquid phase (K_La) was determined in the capillary reactor for several segmented flow conditions (liquid flowrates of 2.0, 6.0 and 10.0 L min^{-1} and gas flowrates of 5.8, 9.0 and 12.4 L min^{-1}). The K_La was quantified by the sulfite method, which measures the oxygen transfer rate (OTR) using a rapid Co^{2+}-catalysed reaction of oxygen with sulfite at the gas-liquid interphase, as evaluated by Munoz and co-workers [36]. It measures the maximum rate of oxidation of sodium sulfite to sodium sulfate resulting from the oxygen transfer from the gas phase to the liquid in which there is no dissolved oxygen. The K_La experiments were performed in duplicate, and the results are given as the average value ± standard deviation from the duplicate assays.

2.5. Hydrophobic compound removal

The capillary bioreactor was inoculated on day one (t = 0) with an equal amount of biomass from a chemostat bubble column fed with hexane, toluene, trichloroethylene and alpha-pinene, and fresh activated sludge from Valladolid wastewater treatment plant, to obtain an initial biomass concentration of 0.2 g dry weight L^{-1}. A mixture of volatile organic compounds (VOCs) was continuously injected to the inlet airstream using a syringe pump (Fisherbrand Model 100). The VOC mixture contained hexane, toluene and α-pinene as model compounds representing air pollutants different in hydrophobicity and biodegradability.

The system was continuously operated at room temperature (20 °C) at a gas and liquid flow of 13.9 L min^{-1} and 8 L min^{-1}, respectively. This resulted in an average gas contact time in the capillary channels of 0.5 s, where the average gas contact time is calculated as follows (Eq. 1):

$$(V_c \times n_c) / (Q_L + Q_g) \quad (1)$$

where V_c the internal volume of the capillary channels (L), n_c the number of capillary channels (-), Q_L is the measured liquid flow rate (L/s), and Q_g the measured gas flow rate (L/s). The liquid was recirculated in a closed loop and demineralized water was added to compensate evaporative water losses. The inlet concentration of the individual VOCs was maintained for 25 days between 5 and 10 mg m^{-3} (Stage I) and between 2 and 5 mg m^{-3} from day 25–100 thereafter (Stage II). Liquid

samples were taken periodically downstream of the recirculation pump to determine the biomass concentration, the bacterial population structure, pH and conductivity.

2.6. Reliability tests

The reliability of the capillary bioreactor for the abatement of VOCs was studied after 6 weeks of steady state operation. Process performance (robustness) was evaluated after three upsets scenarios commonly found in industrial gas treatment systems, and known to often affect the performance of biological gas treatment systems. Upsets were initiated on days 40, 47 and 61, and consisted of (A) 48 h of liquid recirculation interruption (pump stopped simulating a pump failure), (B) 48 h of inlet air interruption (inlet air supply disconnected simulating a fan failure), and (C) 48 h of both liquid recirculation and inlet air interruption (pump stopped and inlet air supply disconnected, simulating a power supply failure). Upset scenario A does not stop the VOCs supply but eliminates mass transfer of the VOCs to the liquid containing the microbes. Scenario B and C involves discontinuing the VOC supply which results in starvation of the microbial community. VOC removal in the capillary bioreactor after each simulated upset was measured every 1.5 h on the first day after restoring normal operating conditions and once per day any day after.

2.7. Analytical methods

VOC concentrations in the inlet and outlet airstreams were measured daily with a GC-FID using Solid Phase Microextraction (SPME) as a preconcentration step (10 min SPME-fibre exposure to the air in a 250 mL glass cylinder installed upstream and downstream of the reactor). The GC-FID (BRUKER-3900) was equipped with an Agilent HP-5MSI capillary column (30 m × 0.25 mm×0.25 μm). The temperatures in the injector and detector were maintained at 150 and 200 ºC, respectively. The oven temperature was set at 40 ºC for 1.5 min, then increased at 10 ºC min^{-1} to 50 ºC, then after 1 min increased at 40 ºC min^{-1} to 250 ºC. Nitrogen at 2.5 mL min^{-1} was used as carrier gas and as make-up gas (25 mL min^{-1}). Hydrogen and air flowrates were set at 30 and 300 mL min^{-1}. The SPME-fibres (CAR/PDMS 85 μm, Supelco) were initially conditioned at 300 ºC for 1 h prior to calibration, and a cleaning run was performed before sampling with the above-described GC-FID method. Standards of the hexane, toluene and α-pinene, prepared in 250 mL glass bulbs, were used for quantification using the above-mentioned preconcentration conditions.

Biomass concentration in the liquid phase was quantified according to Standard Method 2540 D, as well as pH (Crison BASIC-20 +) and conductivity (Crison BASIC-30) [2]. The population structure of the mixed inoculum and biomass present in the capillary bioreactor was determined at the end of Stage I (day 38) and at the end of Stage II (day 100). Genomic DNA was extracted using the MagNA Pure LC DNA Isolation Kit III. Library preparation and Illumina sequencing were performed at the University of Valencia (FISABIO). In brief, library preparation consisted in the generation of 16 S rDNA gene amplicons following the 16 S rDNA gene Metagenomic Sequencing Library Preparation Illumina protocol (Cod. 15044223 Rev.A). The V3–V4 region of the 16 S rRNA gene was amplified using the primers 341 F (50-CCTACGGGNGGCWGCAG-30) and 785 R (50-GACTACHVGGGTATCTAATCC-30) [21]. Index and sequencing adaptors were added to the gene-specific sequences. The amplicons obtained were quantified on a Bioanalyzer DNA-1000 (expected size ~550 bp). After size verification, the libraries were sequenced using a 2x300pb paired-end run (MiSeq Reagent kit-v3 (MS-102–3001)) on a MiSeq Sequencer (Illumina). R packages used for data analysis included Knitr [50], Knitcitations [5], Markdown [1], Biostrings [39] and Vegan: community ecology package [37].

2.8. Chemicals

The liquid in the capillary bioreactor consisted of a mineral salt medium containing KH_2PO_4 (0.7 g L^{-1}), $K_2HPO_4{\cdot}3\ H_2O$ (0.920 g L^{-1}), KNO_3 (3 g L^{-1}), NaCl (0.2 g L^{-1}), $MgSO_4{\cdot}7\ H_2O$ (0.35 g L^{-1}), $CaCl_2{\cdot}2\ H_2O$ (0.026 g L^{-1}) and 2 mL L^{-1} trace minerals solution containing EDTA (0.5 g L^{-1}), $FeSO_4{\cdot}7\ H_2O$ (0.2 g L^{-1}), $ZnSO_4{\cdot}7\ H_2O$ (0.01 g L^{-1}), $MnCl_2{\cdot}4\ H_2O$ (0.003 g L^{-1}), H_3BO_3 (0.003 g L^{-1}), $CoCl_2{\cdot}6$ H2O (0.02 g L^{-1}), $CuCl_2{\cdot}2\ H_2O$ (0.001 g L^{-1}), $NiCl_2{\cdot}6\ H_2O$ (0.002 g L^{-1}) and $NaMoO_4{\cdot}2\ H_2O$ (0.003 g L^{-1}). The chemicals used for mineral salt medium preparation (PANREAC, Barcelona, Spain) had a purity of at least 99.0%, while the VOCs hexane (Sigma-Aldrich, Madrid, Spain), toluene (Panreac, Barcelona, Spain) and alpha-Pinene (Sigma-Aldrich, Madrid, Spain) had a purity of 95%, 99.5% and 98%, respectively.

3. Results and discussion

3.1. Pressure loss

Selection of the capillary channel diameter for the capillary reactor considered mass-transfer in the capillary channel (a better mass transfer leads to smaller reactor size) as well as the pressure losses over the capillary channel (an increased pressure loss results in increased energy requirements, typically the main cost for operating a gas treating bioreactor). The overall pressure drop of a capillary reactor is the sum of the pressure losses caused by the liquid slugs and the air bubbles. The required pressure for passing air through a capillary channel was here experimentally determined for three glass capillary channels (internal diameters 2.4, 3.4 and 5.0 mm) at different gas velocities while the required pressure for passing liquid through a capillary channel was calculated.

The measured pressure losses were lower than 100 Pa m^{-1} for air velocities between 0.1 and 2 m s^{-1}, which are typical gas-liquid superficial velocities required to obtain segmented flow pattern and consistent with those measured by Liu and co-workers [27,30]. The results of the measured pressure losses show that the pressure loss for conveying a certain amount of gas at identical gas velocity is lower when the diameter of the capillary channel is reduced (see Supplementary Fig. S3), this may be explained by the air velocity being more laminar in the smaller diameter channels. The measured pressure drops in glass channels used in this study were in similar range to those measured in silicon tubing as reported elsewhere [23]. Hence, while a smaller diameter capillary channel requires more channels to convey a certain amount of air, the overall pressure loss per meter of channels is lower in smaller diameter channels when conveying gas only.

The total pressure loss per length unit in a capillary channel with air-water segmented flow is caused by several frictions. The most significant pressure loss for small capillary channels is caused by the wall friction of the liquid slug and, in case of vertical channel configurations, by the static head especially at larger diameter channels. The liquid wall friction can be estimated using the Hagen-Poiseuille equation (Eq. 2), while the static head can be calculated using the volume and density of the liquid slugs.

$$dP_{LWF} / L = 32\ \mu\ U_L / d^2 \quad (2)$$

where dP_{LWF} stands for the pressure loss in a capillary caused by liquid wall friction (Pa), L the length of the capillary channel (m), μ the viscosity (Pa s), U_L the superficial velocity of the liquid slug (m s^{-1}), and d the diameter of the capillary channel (m).

Based on the measured pressure loss by the gas (air bubble) and the calculated pressure loss by the liquid (liquid slug), it can be estimated that the total pressure loss per meter capillary channel will range between a few hundred to about thousand Pascal assuming a gas-liquid superficial velocity range of 1–2 m s^{-1}, a G/L ratio of 4, and a channel internal diameter between 2.4 and 5.0 mm. This pressure loss is in the

similar range of conventional gas treatment technologies. The 2.4 mm internal diameter glass channel was therefore selected for the construction of the multi-capillary reactor since the pressure losses would be relatively low.

3.2. Liquid-gas flow mapping

The establishment of the segmented flow regime was determined visually in the capillary reactor containing a bundle of twenty-five 2.4 mm diameter channels. Fig. 1 shows a map of the liquid and gas flow conditions supporting segmented flow. The liquid slug lengths in the capillary channels of the tested capillary reactor system varied between two and about ten times the channel diameter (0.5–3 cm), with no significant redistribution inside the channels, i.e., the slug size was unchanged along the height in the reactor. The segmented flow pattern could be observed relatively easily, although at high gas and liquid velocities, it became difficult to distinguish it from churn flow where small groups of bubbles appear at the rear of the liquid slug (see also Supplementary Fig. S2). The conditions for which segmented flow could be maintained were broad, although more limited when compared to other studies such as [4,18,42] all measured in a single capillary channel at much lower gas and liquid superficial velocities. The difference with our study can be explained by our gas-liquid distributor, which required a minimum gas flow and liquid flow to provide sufficient gas-liquid mixing in the inlet reservoir of the capillary reactor to provide segmented flow consistently in all channels.

Pertinent to obtaining segmented flow is the surface tension which must be dominant over other forces such as gravity. The Bond number (Bo) is the ratio of the gravitational force to the surface tension force (Eq. 3), where a low value of the Bond number indicates that the surface tension dominates in a system.

$$Bo = \rho \, g \, d^2 / \gamma \quad (3)$$

where ρ is the liquid density (kg m^{-3}), g the gravitational constant (m s^{-2}), d the inner diameter of the capillary channel (m), and γ the surface tension (N m^{-1}). Kreutzer and co-workers [26] proposed that a Bo number lower than 3.3 is required to obtain a segmented air-water flow pattern in a single channel. This threshold would be achieved for a capillary channel with an internal diameter of less than about 5 mm while using water and ambient air at room temperature. However, our results showed that additional conditions are required in a multi-channel reactor such as sufficiently high superficial gas-liquid velocities so that adequate gas-liquid mixing and distribution can be achieved in the bottom gas-liquid mixing reservoir.

The impact of the salt media and biomass (compared to demineralized water) on the gas-liquid flow pattern is shown in Fig. 1. The presence of salt as well as biomass reduced in general the range of gas-liquid conditions for which segmented flow could be established, mostly at the lower end of the liquid flow rate and at the higher end of the gas flow rate.

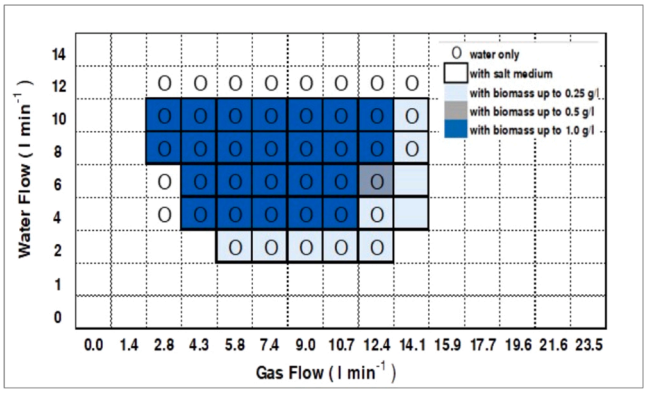

Fig. 1. Occurrence of segmented flow in the capillary reactor in all the twenty-five channels under the different gas flowrate and liquid flowrate conditions using water only, salt medium and biomass additions to the mineral salt medium.

3.3. Mass transfer coefficients

The results of the measurements for gas-liquid mass transfer coefficient (K_La) for oxygen transfer in the capillary reactor under nine different gas and liquid flow conditions are shown in Table 1. The highest K_La value of 462 h^{-1} was recorded at a gas flow rate of 9 L min^{-1} and a G/L ratio of 1.5, which corresponds to an average superficial gas and liquid slug velocity in the capillary channel of 3.2 m s^{-1}, assuming that the liquid wall film thickness is negligible. Values above 400 h^{-1} were all measured at the relatively high gas flow of 12.4 L min^{-1} for all G/L ratios tested ranging from 1.2 to 6.2, corresponding to an average gas contact time in the channel of ~ 0.5 s to ~ 0.7 s, respectively.

Correlating the mass transfer data obtained for the capillary reactor operated under the conditions tested using a continuous stirred tank reactor (CSTR) model similarly to that proposed by Bercic and Pintar [4], results in the following equation (Eq. 4):

$$K_La = 220 \, U_{G/L}^{\ 0.47} / (1 - \varepsilon_G)^{\ 0.18} \quad (4)$$

where K_La is the overall mass transfer coefficient (h^{-1}), $U_{G/L}$ the gas bubble-liquid slug superficial velocity (m s^{-1}) and ε_G the average gas volume fraction (-) in the channels of the capillary reactor (Fig. 2).

The unit length (i.e., gas bubble length + liquid slug length) was non-homogeneous among the twenty-five capillary channels as can be expected, with the average unit length estimated to be about 3 cm, and did not change notably with the conditions tested. The K_La was found to be mostly related by the gas bubble-liquid slug superficial velocity ($U_{G/L}$) and less by the gas-liquid ratio (i.e., the average gas volume fraction ε_G), which is consistent with the observations made by Bercic and Pintar [4], but here defined for a multi-channel reactor under higher flow rates and with liquid containing the salt media. The gas-liquid distribution using a perforated membrane in the capillary reactor in our study made it possible to use multiple capillary channels bundled in one reactor. Nevertheless, it did not allow to control the gas bubble and liquid slug lengths independently, and thus the impact of these individual lengths could not be analyzed.

The overall mass transfer coefficients measured in this study (> 400 h^{-1}) were superior, especially when taking into account the extremely short gas contact time, compared to those reported for conventional biological gas treatment systems, with K_La values ranging typically between 20 and 250 h^{-1} as measured for biotrickling filters or conventional bubble column bioreactors and typically requiring longer gas contact times [7,20,29,40,45].

Table 1
Influence of the gas and liquid flowrate on the oxygen mass-transfer in the capillary reactor. The values are presented as the steady-state average with the corresponding standard deviation (± SD, n = 2).

Liquid Flow (L min^{-1})	Gas Flow (L min^{-1})	G/L Ratio (-)	ε_G (-)	$U_{G/L}$ (m s^{-1})	RT_G (s)	K_La (h^{-1})
2.0	5.8	**2.9**	0.75	1.2	**1.3**	**294 ± 16**
2.0	9.0	**4.5**	0.82	1.6	**0.9**	**328 ± 16**
2.0	12.4	**6.2**	0.86	2.1	**0.7**	**436 ± 16**
6.0	5.8	**1.0**	0.49	1.7	**0.9**	**349 ± 2**
6.0	9.0	**1.5**	0.60	2.2	**0.7**	**462 ± 12**
6.0	12.4	**2.1**	0.67	2.7	**0.6**	**446 ± 7**
10.0	5.8	**0.6**	0.37	2.3	**0.6**	**356 ± 4**
10.0	9.0	**0.9**	0.47	2.8	**0.5**	**369 ± 11**
10.0	12.4	**1.2**	0.55	3.3	**0.5**	**415 ± 12**

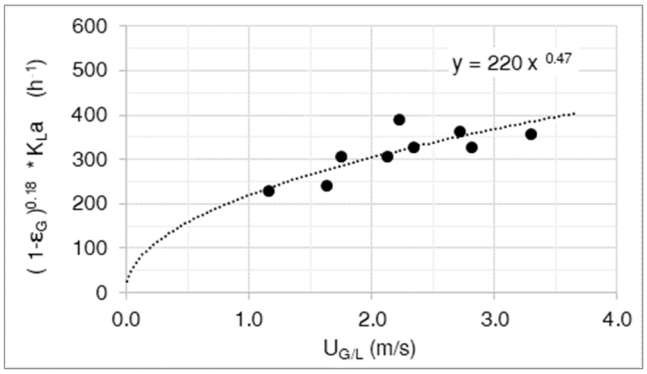

Fig. 2. Correlation of the mass transfer data to the gas bubble-liquid slug superficial velocity ($U_{G/L}$) and the average gas volume fraction (ε_G) of the gas bubble-liquid slug.

3.4. Hydrophobic compound removal

Continuous treatment of the hydrophobic pollutants was established in the capillary bioreactor at an air flow and liquid flow of 13.9 L min^{-1} and 8 L min^{-1}, respectively, which corresponds to a gas contact time of 0.5 s in the capillary channel. Operation and performance were stable without replenishing the liquid in the reactor; the pH of the recirculating liquid remained at 7.6 during the entire experiment (100 days), which suggested that no acidic or alkaline (potentially toxic) metabolite accumulated.

A significant removal of the three VOCs was observed after inoculating the capillary bioreactor (Fig. 3), with a gradually increasing toluene removal during the first two days indicating growth or acclimation. The removal efficiencies of hexane, toluene and α-pinene averaged 58 ± 10%, 90 ± 5% and 30 ± 12%, respectively, during Stage I. The lowering of the inlet VOC concentration (day 25) did not significantly change the removal efficiency of hexane or toluene, which were on average 57 ± 6% for hexane and 92 ± 8% for toluene during Stage II. In contrast, the average removal of α-pinene increased from 30 ± 12% during Stage I to 46 ± 15% during Stage II, while, in general, a less consistent removal was observed for α-pinene.

The VOC removal efficiencies observed were high considering that the gas contact time in the capillary channels was only 0.5 s, and that the inlet VOC concentrations were low, which reduced the driving force for mass transfer from the gas to the liquid as illustrated by Eq. 5:

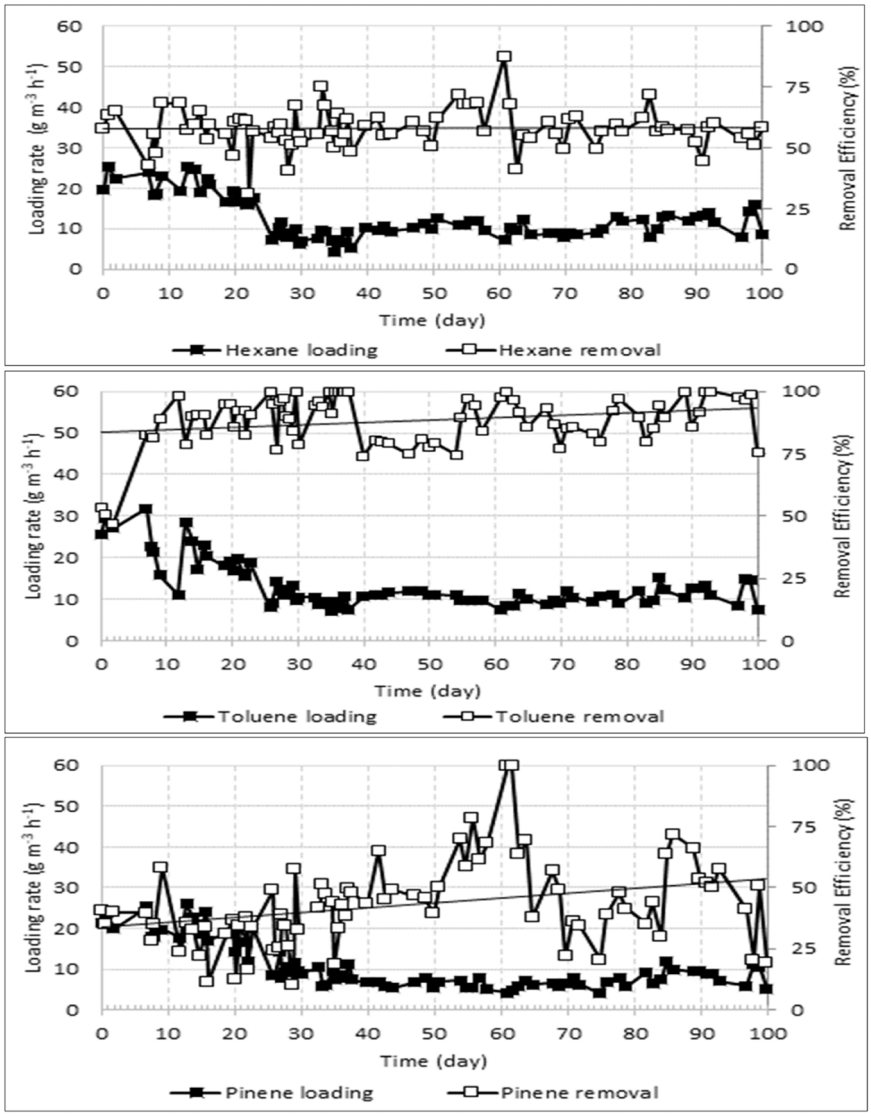

Fig. 3. Time course of the loadings rate (■) and removal efficiencies (□) of hexane (A), toluene (B) and α-pinene (C) in the capillary bioreactor during Phase 1 (day 0 – 25) and Phase 2 (day 25 – 100). The straight line shows the overarching trend of the removal efficiency during the 100-day testing period.

$$R = K_L a\ (C_G/K_H - C_L) \quad (5)$$

where R is the mass transfer rate (g m^{-3} h^{-1}), $K_L a$ the overall mass transfer coefficient for each VOC (h^{-1}), C_G the pollutant concentrations in gas (g m^{-3}), K_H Henry-coefficient (dimensionless) and C_L the pollutant concentrations in the liquid phase (g m^{-3}) [22].

Of the three model VOCs tested, toluene has the lowest dimensionless Henry-coefficient ($K_H = 0.5$) and was removed consistently better than hexane and α-pinene, confirming that K_H is a determining factor for mass transfer. However, α-pinene has a lower dimensionless Henry-coefficient (K_H) than hexane (5 versus 71), meaning gas α-pinene is significantly better absorbed in water and thus more bioavailable than hexane at equal gas concentration. Moreover, α-pinene has a higher octanol-water partitioning coefficient ($K_{o/w}$) than hexane (4.5 vs. 3.1). The octanol-water partition coefficient is commonly used to classify the hydrophobicity of a compound and has been recognized as an indication of the uptake of a pollutant into biological membranes. In addition, presence of biomass in the liquid can influence the Henry-coefficient as discussed by Barton and co-workers [3] and they recommended the use of $K_{o/w}$ rather than the K_H to calculate mass-transfer from gas to water – biomass mixtures. Although the authors showed that the use of $K_{o/w}$ does not always predicts the correct mass-transfer value, they observed that the effect of biomass on the Henry coefficient (trend and order of magnitude) is described correctly. In our study, both K_H and $K_{o/w}$ do not explain why hexane was better removed than α-pinene and may suggest that α-pinene removal was hampered by biokinetic limitations.

The biodegradation of α-pinene may be more complex due to its larger molecular weight and its different (cyclic) structure than hexane. The biodegradation of α-pinene may involve its partial enzymatic conversion outside the bacterial cell into smaller compounds that can then be taken up more readily by the bacterial cells, according to the mechanism proposed by Miller and Allen [34].

The capillary reactor set-up contained an inlet reservoir (gas-liquid mixing zone) and the outlet reservoir (gas-liquid disengagement zone), and it can be assumed that most of the biodegradation takes place within the reservoirs (as they hold most of the liquid containing the biomass). It can also be assumed that nearly all the gas-liquid mass-transfer takes place inside the capillary channels as the air bubbles are relatively large (estimated about 0.6 cm in diameter on average). Nevertheless, the experimental setup was chosen for practical reasons and scaling-up the capillary bioreactor system would require a more optimized configuration of the reservoirs (with a reduced liquid height) to minimize the hydrostatic pressure losses across the liquid phases.

3.5. Bioreactor reliability tests

Reliability is the combination of robustness and resilience, where robustness reflects the capacity of a system to maintain its functionality when subjected to changes. The resilience is the rate at which a system returns to its original state after being perturbed. Both the robustness and resilience were tested for three common upset scenarios likely to occur in actual biological gas treatment systems: water pump failure, air fan failure and power supply failure. The results showed that both upset test A (the 48-hour interruption of the liquid recirculation) and upset test B (the 48-hour interruption of the air supply) impacted the removal of toluene only: removal of toluene dropped from steady state values $>$ 95% to about 80% immediately after restoring liquid recirculation. Two weeks were needed for the capillary bioreactor system to fully recover preceding toluene removal capacity. It is interesting to note that the third upset test two weeks later (upset test C: stopping both the liquid recirculation and the air supply) did not impact the removal of toluene. This seems to indicate an increased robustness of the biomass community towards liquid recirculation and air supply interruptions after being exposed a few weeks before to upset A and B. None of the upset tests did negatively affect the removal of hexane and α-pinene. Upset test C resulted in a temporary increase of the removal of α-pinene from 65% to about 100% the first day after restoring the normal operation conditions and may be explained by a transient sorption effect.

Relevant to long-term stability of the process is the observation that segmented flow in the capillary bioreactor could be maintained throughout the 100-day study. Overall, these results show that stable operation and performance of the capillary bioreactor could be maintained over extended periods of time and was not significantly affected by the tested upsets.

3.6. Microbial characterization

The biomass content was on average 0.25 ± 0.06 g dry weight L^{-1} and increased during 100-days of operation of the bioreactor from 0.20 g L^{-1} (day 1) to 0.29 g L^{-1} (day 100). This indicates that biomass can be sustained in a capillary bioreactor even at the relatively low inlet VOCs concentrations tested in this study. The successful application of capillary bioreactor systems for air pollution control also requires absence of clogging of the individual capillary channels with biomass over time. No signs of biomass accumulation in any of the capillary channels were observed during the 100-days operation with the biomass in the bioreactor a suspended cell culture. This observation is consistent with the findings of Lopez de Leon and co-workers [31] who also did not observe biofilm formation inside capillaries when operated at higher VOC concentrations favorable to biomass growth. This is also consistent with Studer [47] showed that biofilm accumulation could easily be controlled with relatively low shear forces. Thus, it is likely that the high recirculating liquid velocity inside the capillaries caused sufficient shear to prevent biomass accumulation.

Biological characterization of the cultures involved revealed that high-quality filtered reads were obtained after sequencing of the V3–V4 region of the 16 S rRNA gene in the different biomass samples of the inocula and bioreactor culture broth. The rarefaction curves reached the plateau, indicating that the sequence depth was sufficient to represent the diversity of the bacterial community in the samples (Fig. 4A). The diversity of the bacteria in the capillary reactor on day 38 and day 100 was around 300 Operational Taxonomic Units (OTUs), with an OTU the operational definition commonly used to classify groups of closely related species.

Cluster analysis showed a clear separation of the structure of microbial communities between the inoculum samples and the samples collected from the capillary bioreactor (Fig. 4B). Interestingly, the observed bacterial diversity of the samples based on Shannon index values was markedly high in the capillary bioreactor samples (Fig. 4C). Despite the high diversity of the Inoculum-Activated Sludge sample, the composition of the bacterial community drastically changed in the capillary bioreactor (Supplementary Fig. S4), most probably because of the different substrates used for bacterial growth resulting in different selective pressure. The high diversity may also be key to support the resilience of the microbial communities towards perturbations, which may explain the high robustness of the capillary bioreactor against the upset scenarios applied [14,43,44].

Overall, Proteobacteria and Bacteroidota represented the dominant phyla in both capillary bioreactor samples, followed by Actinobacteria, Planctomycetota, Verrucomicrobia, Chloroflexi and other less represented phyla (Supplementary Fig. S4). The relative abundance of members of Actinobacteria, Bacteroidota and Chloroflexi increased after the reliability tests applications, suggesting their ability to better cope with the tested upsets.

4. Conclusions

A multi-channel capillary bioreactor was studied for the continuous treatment of hydrophobic VOCs. This work revealed that the overall mass transfer coefficient typically increased most with the gas superficial velocity ($U_{G/L}$) at each liquid flow tested and increased somewhat with gas volume fraction (ε_G). At the highest gas flow tested, $K_L a$ values above 400 h^{-1} were measured for a wide range of gas to liquid ratios. At

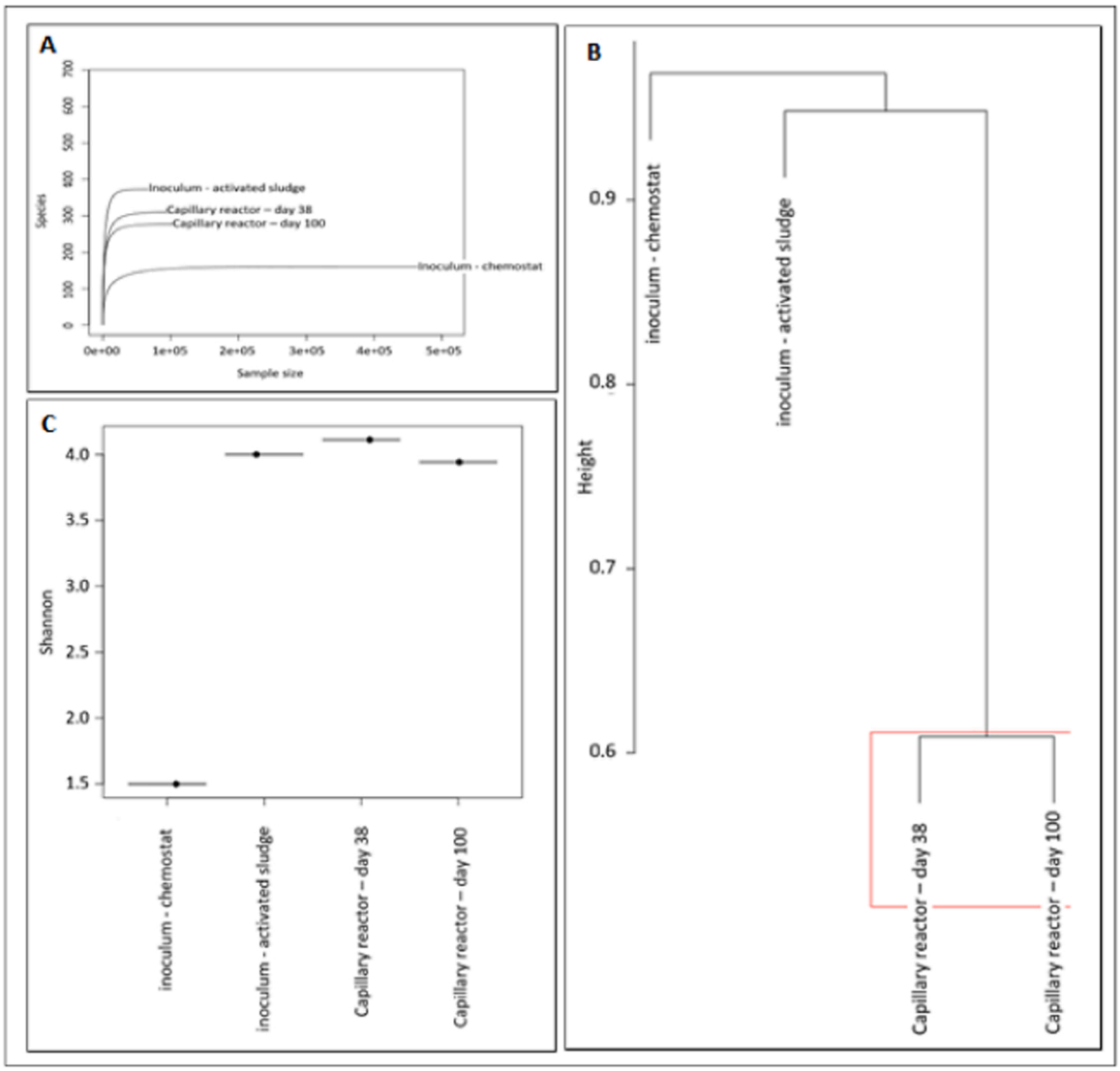

Fig. 4. The biological characterization of the cultures involved illustrating the rarefaction curves of OTUs (A), the hierarchical cluster dendrogram of bacterial communities; the height axis displays the distance between observations and/or clusters; the horizontal bars indicate the point at which two clusters/observations are merged (B), the Shannon diversity index values (C).

only 0.5 s of gas contact in the channels, the removal efficiency of the model air pollutants hexane, toluene and α-pinene was on average 58%, 90% and 44%, and up to about 75%, 99% and 75%, respectively. This extreme low gas contact time is at least one but closer to two orders of magnitude less than conventional biological air treatment systems even if the wall thickness of the capillary channels would be considered. An active pollutant-degrading culture could be sustained in the system and no accumulation of biofilm inside the capillary channels was observed. The bioreactor system showed stable operation for 100-days and was robust against three common upset scenarios, possibly facilitated by the highly diverse bacterial community that was observed. Overall, this work opens new opportunities for expanding the application field of biological processes to control emissions of air pollutants.

CRediT authorship contribution statement

Norbertus Kraakman: Conceptualization, Methodology, Investigations, Writing – original draft. **Javier González-Martín:** Investigations, Resources. **Cristina Pérez**: Investigations. **Elisa Rodríguez:** Data curation, Writing. **Raquel Lebrero**: Supervision, Writing – review & editing. **Marc Deshusses**: Writing – review & editing. **Raúl Muñoz:** Supervision, Writing – review & editing.

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

No data was used for the research described in the article.

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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.2023.110502.

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