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A capillary bioreactor to increase methane transfer and oxidation through Taylor flow formation and transfer vector addition

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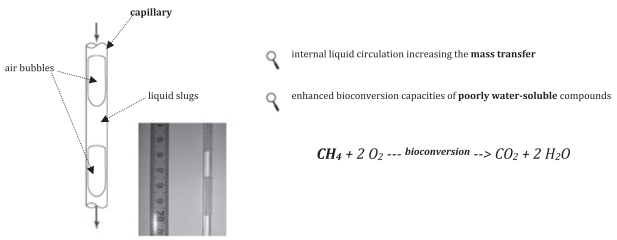
HIGHLIGHTS

- We studied methane oxidation in a capillary gas treatment bioreactor.
- A new bioreactor in which Taylor flow with transfer vector addition are combined.
- Superior mass transfer (k_La) is obtained when compared to conventional bio-contactors.
- Improved methane removal obtained when compared to conventional bio-contactors.
- A method demonstrated to improve bio-treatment of gaseous hydrophobic compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

The impact of two strategies to enhance the mass transfer of hydrophobic compounds, Taylor flow (or segmented flow) and the addition of an organic transfer vector (silicone oil), were investigated under abiotic and biotic conditions in a capillary bioreactor. The capillary bioreactor consisted of a capillary column (where Taylor flow was produced in a gas/liquid flow) and a gas–liquid separator at the outlet of the capillary column which was operated as a stirred tank with superficial aeration. It was shown that the system was limited by mass transfer and not by the biological reaction. Taylor flow in the capillary resulted in an increase of up to two orders of magnitude for the volumetric oxygen transfer coefficient (k_La) when compared to the coefficient for the gas–liquid separator, or values previously obtained in other turbulent contactors. The bioconversion rates of methane in the capillary column where found to be significantly higher than for conventional systems. Silicone oil addition increased k_La up to 38% in the gas–liquid separator, but reduced it with 38% in the capillary. Contrary to observations during abiotic k_La determinations, silicone oil addition increased the CH_4 removal and O_2 consumption by the methanotrophic consortium in both, gas–liquid separator and capillary. Increased gas flow rate gave an 19% increase in methane removal in the capillary bioreactor, an additional increase of 8% was obtained adding 5% of silicone oil at the same flow, while an additional increase of 47% was obtained adding 10% of silicone oil at the same flow with inoculum pre-adapted to transfer vector. The contribution of the capillary channel to the overall methane removal in the system was high considering that the volume of this channel was just 0.64% of the total volume in the bioreactor, indicating a good potential of further optimization of the reactor system.

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1. Introduction

Biodegradation of poorly water-soluble air pollutants, such as methane, is in applied biological gas treatment systems generally limited by the mass transfer from the gas to the aqueous phase where the microorganisms are present [1]. A strategy to increase the mass transfer of hydrophobic compounds in air treatment applications is the addition of an organic phase (solid or liquid) with more affinity for the target compound than water [2]. The systems amended with the organic phase are called in generic way two-phase partition bioreactors (TPPBs) and the organic phase is known as *transfer vector*. TPPBs have shown to improve toluene [3], hexane [4], and methane removals [5]; the oxygen transfer rate [6–8], and the performance under transient conditions [9,10].

In turbulent systems (stirred tank and airlift reactors) the transfer vectors can increase the gas/water interfacial contact area (a) by disruption of the gas bubbles as shown by Galindo et al. [11] and Quijano et al. [12]. Also, the driving force for mass transfer is increased by the higher solubility of the hydrophobic compounds in the organic phase (up to 10 times more for methane and oxygen in silicone oil than in water) as shown by Rocha-Rios et al. [5]. Finally, it is possible that the microorganisms extract the pollutants *directly* from the vector, without intermediate transfer to water as suggested by McLeod and Daugulis [13] and Rocha-Rios et al. [5,8]. These three mechanisms explain the observed higher degradation velocities in stirred tanks added with a vector transfer.

Higher degradation rates alone, however, are not sufficient. The effectiveness of the transfer vector, in economical rather than process-dynamical terms, depends on the cost of the vector, which is usually expensive [14]. Moreover, dispersing the vector in water requires energy [1]. Both the increased power consumption in the system [8,15] and the organic phase cost severely impede the application of these systems on a commercial scale. For highly soluble compounds, dispersion and mass transfer are less important and in that case classical laminar bioreactors (biofilters, biotrickling filters and bioscrubbers) have adequate performance.

Laminar contactors such as biofilters, biotrickling filters and bioscrubbers, with commercially attractive low power consumption, typically have removal efficiencies, for soluble compounds, above 90% [16]. In contrast, when these systems are used for the removal of poorly water-soluble compounds, the removal efficiency can be as low as 40% even at residence times of several minutes [5]. It is questionable if the addition of a vector helps to improve mass transfer in these systems. Without the energy input to break up a transfer vector as silicone oil into small droplets, one obtains in general a non-homogeneous poor dispersion. The benefit of adding a vector in such systems is therefore inconclusive [17].

Another novel strategy to increase gas–liquid mass transfer is the monolithic reactor. Monolith reactors are increasingly significant as multiphase reactors, considering the advantages that they offer in comparison to conventionally used bed and slurry systems for a host of processes. These advantages, which include low pressure drop, high gas–liquid mass transfer rates, and minimum axial dispersion (plug flow), stem from the uniquely structured multichannel configuration of monoliths [18,19]. In essence, a monolith block is composed of an array of uniformly structured parallel channels, often of square or circular geometry, typically having hydraulic diameters between 1 and 5 mm. Thus, the monolith can be viewed as a structure that is comprised of many repeating building blocks, where the basic building block is a single channel. It can be argued that data obtained from studies on a single channel, or what may be called a capillary, can be used in scaling up a monolith reactor, provided that a uniform gas and liquid distribution (such as that obtained) occurs in the monolith block [20,21].

Among several possible flow patterns in capillaries, segmented flow (Taylor flow), gives the best mass transfer properties [22]. In this flow pattern, the flow through the capillary channel consists of liquid slugs well separated from each other by distinct gas bubbles. This flow recirculates within the liquid slugs and increases the mass transfer from the gas to the liquid [23]. Taylor flow in capillaries makes it possible to obtain mass transfer coefficients equivalent to stirred tanks, but with one order of magnitude lower power consumptions or in other words, k_La one order of magnitude higher than stirred tank reactors for the same power consumption [21].

Monolith packages have recently gained importance in biotechnological applications as relatively high mass transfer rates can be obtained at relatively low energy input [1,21]. Ebrahimi et al. [24] and Ebrahimi et al. [25] studied the possible clogging of the channels by biomass growth, while Jin et al. [26] used a monolith bioreactor to treating air polluted with volatile organic compounds (VOCs). Monoliths are often operated at higher superficial velocities than trickle beds, and the residence time may be too short to achieve full conversion in a single pass [27].

In this work the effects of Taylor flow and the addition of a transfer vector on methane biodegradation in a capillary bioreactor were studied compared to a control system without these tested variables. This is the first report of methane oxidation in a capillary bioreactor, and moreover it is the report of a bioreactor with both Taylor flow and the transfer vector addition. The aim of this work was to investigate the feasibility of two-phase partition capillary bioreactors to extent the application field of biological air treatment.

2. Materials and methods

2.1. Microorganisms and culture conditions

A methanotrophic community (with *Methylobacterium organophilum* as the predominant strain) was enriched from an activated sludge sample at UAM-Iztapalapa wastewater treatment plant (México City). Culture maintenance, inoculum preparation and mineral salt medium composition were carried out as previously described by Rocha-Rios et al. [5].

2.2. Chemicals

Natural gas with an average methane concentration of 93% was diluted with air to obtain an average methane concentration of 4.2% (v/v) or 32 g m^{-3}. Silicone oil (polydimethylsiloxane) with 100 cSt of kinematic viscosity (S100) was purchased from Sigma–Aldrich. Silicone oils are not biodegraded or toxic for this methanotrophic community as shown by Rocha-Rios et al. [28].

2.3. Experimental set-up

The diagram of the system used for methane oxidation experiments is shown in Fig. 1. The capillary bioreactor consisted of an acrylic tube (polymethylmetacrylate) of 1 m of length and 0.003 m of inner diameter. A gas–liquid contactor similar to that described by Simmons et al. [29] was used to minimize the pressure shock during the contact in the entrance of capillary. The biphasic flow in the capillary was co-current downward. The gas was recirculated in a closed loop using an oil-free diaphragm pump (Wisa, Germany). The liquid was recirculated using two peristaltic pumps (Cole–Parmer, USA) connected in parallel to reduce the pulsations. The gas flow through the capillary was controlled with a rotameter and a needle valve. A jacketed flask with magnetic agi-

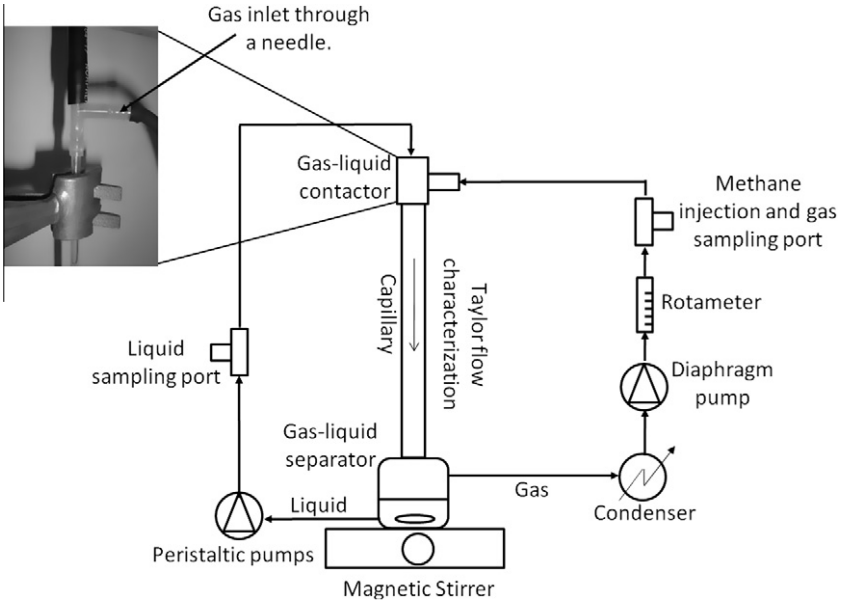

Fig. 1. Experimental set-up for methane biodegradation experiments.

tation adapted at the bottom of capillary permitted the gas and liquid separation previous to recirculation as well as the homogenization of the liquid phase. The temperature of the flask was controlled circulating water at 30 °C (water bath MGW Lauda M3, Germany). A condenser with cooling water at 10 °C (cryostat WK230 Lauda, Germany) placed at the outlet of the gas–liquid separator prevented water evaporation towards the diaphragm pump. The total volume of liquid in the capillary bioreactor during all the experiments was 300 mL.

2.4. Sulfite oxidation method for OTR determination

The oxygen transfer rate (*OTR*) was determined in the capillary bioreactor using the sodium sulfite oxidation method as described by Quijano et al. [14] at different gas and liquid flow combinations (Taylor flows) and with and without vector presence. In this method the oxygen reacts instantaneously with sodium sulfite so the oxygen concentration in the liquid is zero (maximal gradient).

$$OTR\ (\mathrm{mg\ L^{-1}s^{-1}}) = \frac{dC_{O_2}}{dt} = k_L a\left(C^*_{O_2} - \cancel{C_{O_2}}^{0}\right) = k_L a\left(C^*_{O_2}\right) \quad (1)$$

where $C^*_{O_2}$ and C_{O_2} are the saturation and dissolved oxygen concentrations (mg L^{-1}) in the liquid phase, respectively.

To include the increase in $C^*_{O_2}$ by the vector presence in the liquid (emulsion), a volumetric average function was used [8].

$$C^*_{O_2} = \phi C^*_{O_2W} + \theta C^*_{O_2O} \quad (2)$$

where ϕ and θ are the volumetric fractions of water and oil, respectively (dimensionless). $C^*_{O_2W}$ and $C^*_{O_2O}$ are the concentrations of oxygen saturation for water and oil, respectively (mg L^{-1}).

By stoichiometry, the mass of oxygen that reacted with sodium sulfite (transferred to the liquid) is obtained, which expressed per volume of sample produces the oxygen concentration absorbed in the liquid (C_{O_2}). A graph of C_{O_2} from the different samples *versus* time produces a straight line with *OTR* as slope. Finally, dividing *OTR* by $C^*_{O_2}$ we obtained k_La (s^{-1}).

2.5. Abiotic mass transfer experiments

For these experiments the system shown in Fig. 1 was slightly modified and operated as semi-closed loop introducing continuously dry air through the capillary with a mass flow controller (Brooks Instruments, The Netherlands) and circulating the liquid with a four channel Ismatec® pump equipped with six-rollers for precise control of gas and liquid flows. Initially, *OTR* was determined in the overall system (capillary and gas–liquid separator), and then under the same flow conditions in the gas–liquid separator only, which was considered as a stirred tank with superficial aeration introducing the gas through the capillary and the liquid by an independent port at the top of the separator.

OTR_{cap} was determined from OTR_{over} and OTR_{sep} through a mass balance as expressed in following equation:

$$OTR_{cap}(V_{liqcap}) + OTR_{sep}(V_{liqsep}) = OTR_{over}(V_{liqover})\ [\equiv]\ \mathrm{mg\ s^{-1}} \quad (3)$$

where V_{liqcap}, V_{liqsep} and $V_{liqover}$ are the liquid volumes (in liters) of capillary, gas–liquid separator and overall, respectively. V_{liqcap} was obtained multiplying the channel's volume (V_{cap}) by the average liquid holdup (ε_{liq}) in the segmented flow.

The corresponding values of k_La for the overall system, separator and capillary were obtained dividing *OTR* by $C^*_{O_2}$ (from Eq. (1)). All the experiments were carried out in duplicate testing two Taylor flows and two vector fractions.

2.6. Methane biodegradation experiments

Once the system (Fig. 1) was inoculated, the biodegradation experiments were performed in batch, injecting 100 mL of natural gas in the closed gas loop of the system to obtain the initial desired methane concentration (≈4.2% v/v). The duration of each experiment was one day and periodic samples of gas were used to measure the time course of CH_4, O_2 and CO_2 concentrations by TCD-GC while periodic samples of liquid permitted monitoring the biomass and pH evolution. As described for the mass transfer experiments, the methane removal rate ($-rCH_4$) was measured in the overall system and in the gas–liquid separator. Each condition of Taylor flow (with or without transfer vector) tested in the system, was performed in triplicate (three kinetics) to warrant experimental

Table 1
Liquid (L) and gas (G) flows, Taylor flow presence in the system, and silicone oil fraction (θ) during the methane oxidation experiments.

Condition	L (mL min^{-1})	G (mL min^{-1})	Taylor flow presence[A]	θ (%)
1	77.3	50	+	0
2	77.3	50	–	0
3	77.3	150	+	0
4	77.3	150	–	0
5	77.3	150	–	5
6	77.3	150	+	5
7[B]	77.3	150	+	10

[A] + or – represent if the system was operated using the overall system (capillary and gas–liquid separator, +) or just the gas–liquid separator (–), respectively.
[B] This was an exploratory experiment with inoculum from the same source but preadapted previously to S100 (10% v/v) in serological bottles.

reproducibility. Table 1 summarizes the experimental conditions tested during the methane oxidation experiments.

Similarly to the mass transfer experiments, the methane removal rate in the capillary was obtained in triplicate for two Taylor flows and two vector fractions from a mass balance (Eq. (4)), considering the methane removal rates in the overall system and in the gas–liquid separator independently.

$$-rCH_{4cap}(V_{gascap}) - rCH_{4sep}(V_{gassep}) = -rCH_{4over}(V_{gasover}) \ [\equiv] \ g\ h^{-1} \quad (4)$$

where V_{gascap}, V_{gassep} and $V_{gasover}$ are the gas volumes (m^3) of capillary, gas–liquid separator and overall, respectively. V_{gascap} was obtained multiplying the channel's volume (V_{cap}) by the average gas holdup (ε_{gas}) in the segmented flow.

2.7. Analytical procedures

Gaseous CH_4, CO_2 and O_2 concentrations were measured in duplicate using a GC-TCD (Varian 3800, The Netherlands) equipped with a Molecular sieve 13 × 80/100 Mesh 1.2 × 1/16″ × 1 mm Ultimetal® column. Helium was used as a carrier gas at a flow rate of 0.2 mL min^{-1}. The temperature of the detector and injector were maintained at 200 °C, respectively and the oven temperature was maintained at 50 °C. External standards enabled CH_4, CO_2 and O_2 quantification.

Biomass concentration in the reactor was measured in duplicate via culture optical density determinations at 600 nm (OD_{600nm}) using a Hach Lange DR2800 spectrophotometer (UK) and with a correlation previously obtained of OD_{600nm} as a function of cells' dry weight (DW). The pH value in the system was periodically monitored using pH test strips with a range from 6.5 to 8.5 (Yercon, China).

2.8. Statistical analysis

All results are given as the mean value with their corresponding standard error. For comparison, the results of the different tested conditions were analyzed using one-way ANOVA with significance at $p \leqslant 0.05$. The NCSS® statistical package was used for data analysis.

3. Results and discussion

3.1. Taylor flow characterization

The various flow patterns that were observed inside a 3 mm capillary for different superficial velocities of gas (*Usg*) and liquid (*Usl*) are reported in Fig. 2. In our reactor, Taylor flow was observed for a wide range of flows. When the gas flow was significantly smaller than the liquid flow, small bubbles were observed (bubbly flow) instead of the channel-filling Taylor bubbles. When the gas flow rate was significantly higher than the liquid flow rate, a chaotic churn flow was observed that lacked the regular characteristics of segmented flow. Between these two regimes, Taylor or segmented flow was present with large gas bubbles and liquid slugs. This flow regime map is consistent with reports from other authors [18,19].

The average dimensions of the gas bubble and water slug in the segmented flow ranged from 0.5 and 1.5 cm, respectively (at minimal *Usg* and minimal *Usl*) up to 4.5 and 6 cm, respectively (at maximum *Usg* and maximal *Usl*).

3.2. Abiotic mass transfer experiments

Fig. 3 summarizes the results of the volumetric mass transfer coefficient (k_La) for the overall system, the gas–liquid separator and the capillary channel, which were estimated from *OTR* determinations (Eq. (3)) by sulfite oxidation method with two different Taylor flows and two different vector fractions.

k_La_{cap} was estimated from Eq. (3) between 1 and 2 s^{-1} (Fig. 3) which was two order of magnitude higher than k_La_{sep} (0.01–0.02 s^{-1}). In a previous study [28], abiotic k_La values between 0.01 and 0.06 s^{-1} were determined in an airlift bioreactor using the same method for the experimental determination, while Quijano et al. [7] reported values between 0.01 and 0.06 s^{-1} for two turbulent contactors, airlift and stirred tank reactors. Kraakman et al. [1] compared k_La values estimated by Kreutzer et al. [19] for the monolithic reactor with those measured in two biotrickling filters by Kim and Deshusses [30] and determined an improvement of 1.5 orders of magnitude in the monolith. This is consistent with the order of magnitude analysis from Kreutzer et al. [21] where k_La in monolithic reactors was estimated between one or two orders of magnitude higher than in bubble columns and stirred tank reactors. This means that the capillary channel produced k_La values higher than those obtained in the gas–liquid separator, but with a liquid volume lower than 1% of the overall liquid volume in the system. The contribution of the capillary channel to the overall mass transfer in the bioreactor was from 37% to 56% which shows the potential of capillary bioreactors to increase mass transfer of poorly water soluble compounds.

3.2.1. Taylor flow effect on k_La

Results in Fig. 3 suggest an increase in k_La for both capillary and gas–liquid separator increasing the superficial velocity of gas in the Taylor flow (with and without S100). Increasing the gas flow from 20 to 70 mL min^{-1} without S100 resulted in k_La increases of 11% and 38% in the gas–liquid separator and capillary, respectively. With S100 (10% v/v) the increase in the gas flow produced k_La enhancements of 11% in the gas–liquid separator and 19% in the capillary.

3.2.2. S100 addition effect on k_La

3.2.2.1. Gas–liquid separator. k_La increases of 38 and 11% at 20 and 70 mL min^{-1}, respectively, were determined in the gas–liquid separator adding the mass transfer vector (Fig. 3). These results are consistent with other reports where silicone oil with different viscosities has increased the mass transfer of poorly soluble compounds in turbulent bioreactors [7,8,31]. It is important to underline that the gas–liquid separator was operated as a stirred tank with superficial aeration. Silicone oil has shown impacting positively k_La in turbulent contactors through two main effects, (1) by increasing the bioavailability of hydrophobic compounds due to the higher solubility in the liquid phase where microorganisms are present, because of a lower dimensionless partition coefficient ($H = C_G/C_L$) in the emulsion than in water [28]; and (2) the

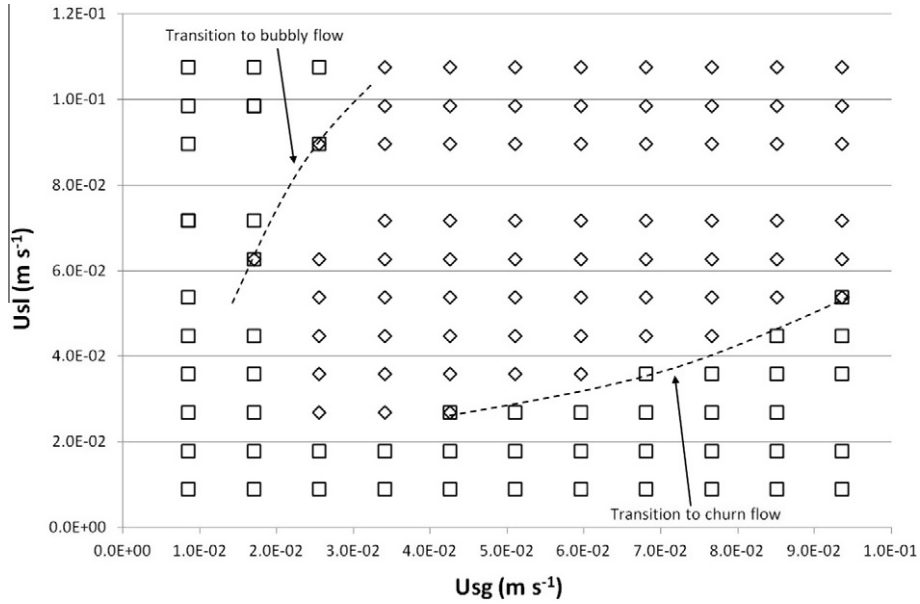

Fig. 2. Gas (*Usg*) and liquid (*Usl*) superficial velocities where Taylor (◇) or other kind of flows (□) were obtained in the acrylic capillary with 3 mm of inner diameter.

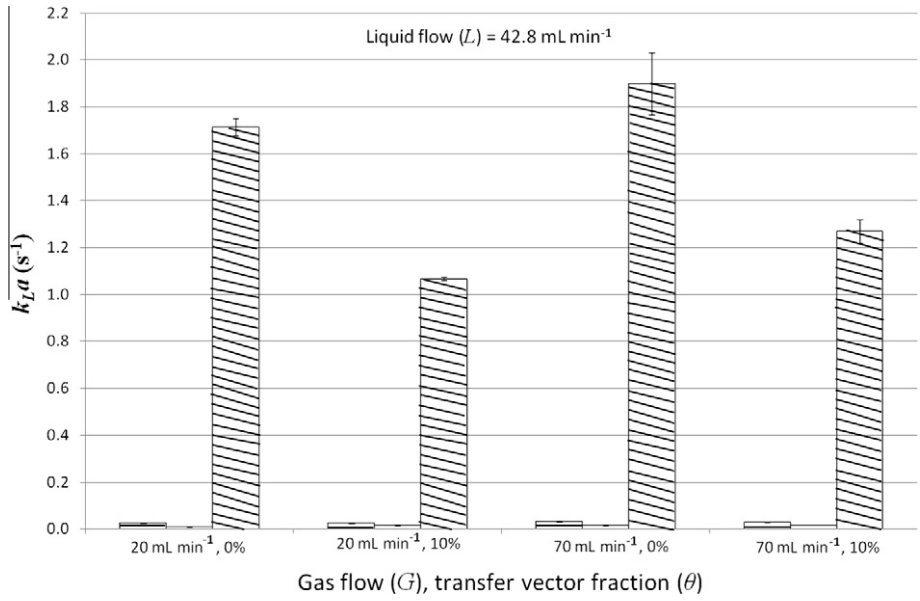

Fig. 3. Abiotic k_La determinations in the overall system (⊟), gas–liquid separator (□) and capillary (◹) for two Taylor flows and two S100 fractions by the sulfite method.

dispersed oil drops reduce the size of the gas bubbles colliding with them and by a reduction in the surface tension between gas and liquid and thus increasing the interfacial contact area (a) [12].

3.2.2.2. Capillary channel. In the laminar gas–liquid contactor (capillary channel), unexpected reductions in k_La of 38% and 33% at 20 and 70 mL min^{-1}, respectively, were determined with addition of S100 (10% v/v) (Fig. 3). In these experiments, the oil drops were well dispersed in the water slugs and the average bubble size determined was smaller with presence of S100, increasing the specific contact area a through the channel (data not shown). Therefore, the negative impact of S100 should be localized on k_L.

k_L depends on the diffusion coefficient (D) in the emulsion. D in turn depends on the viscosity μ through the Stokes–Einstein relation $D = kT/6\pi\mu r$, the viscosity of pure S100 on Taylor flow is 100 times higher than that of water. Considering the oil and water fractions and a perfectly mixed emulsion, the kinematic viscosity (μ/ρ) of the liquid phase would be approximately 5.8×10^{-3} m^2 s^{-1}, where the corresponding kinematic viscosity of water is just 8×10^{-7} m^2 s^{-1}. The viscosity of the emulsion not only impacts diffusion. The pressure drop is also increased. Moreover, specifically for segmented flow, the thickness of the film between the bubble and wall increases, with possible implications for mass transfer when the oxygen can penetrates all the way to the wall [32]. These negative effects are naturally also present in the turbulent contactors; however, the positive effects described above can overpass them by increasing the power consumption as was reported by Rocha-Rios et al. [8] who observed no enhancement on mass transfer with silicone oil addition (10% v/v) in a stirred tank at 200 rpm, but when the stirring rate was increased at 500 and 800 rpm, increases on k_La were measured. Galindo et al. [11] observed in a stirred tank that direct contact between oil drops and gas bubbles was an important

pathway of gas–liquid mass transfer. In segmented flow where the oil drops are dispersed in the water slugs there is not such direct contact between gas and organic phase.

3.2.2.3. Overall system. Other important result shown in Fig. 3 is that k_La_{over} was approximately constant with and without S100 addition for both Taylor flows tested because the decrease on k_La_{cap} was offset by the increase on k_La_{sep}. More experiments are however required to determine the real impact of the transfer vector on the Taylor flow hydrodynamics and consequently on the capillary's mass transfer.

3.3. Methane biodegradation experiments

At the beginning of the biological experiment, we first verify that methane removal in the system was limited by mass transfer and not by the activity of the microorganisms. A biomass pulse that doubled the cell concentration was added to the system concluding the kinetics at day seven. This addition did not lead to a twofold increase in methane oxidation (Fig. 4) as expected, and the system was clearly not limited by biological conversion capacity. Rather, mass transfer was limiting. The suspended biomass concentration varied between 0.3 and 0.8 g L^{-1} through the experiment.

The average rates of methane removal ($-rCH_4$), CO_2 production (rCO_2) and O_2 consumption ($-rO_2$) through the experiment are summarized in Table 2 for each tested condition of Taylor flow and oil fraction listed in Table 1.

A carbon balance indicated a 70% minimum of carbon from CH_4 oxidized to CO_2 (Table 2) suggesting a carbon assimilation as biomass lower than 30% which is agree with the yield of biomass' production per gram of methane consumed obtained previously for these cells ($Y_{X/CH4}$ = 0.49 ± 0.02 g g^{-1}) [28]. One-way ANOVA analysis was used to determinate significant differences between the average rates of methane oxidation obtained for each condition indicated in Table 1.

In the discussion that we present below, we focus on the CH_4 biodegradation, but similar observations can be made from the O_2 consumption and CO_2 production. Fig. 5 summarizes the methane removal rates observed in the overall system, gas–liquid separator, and capillary (estimated from the mass balance in Eq. (4)). As in the mass transfer experiments the methane removal rate in the capillary was approximately two orders of magnitude higher than in the gas–liquid separator, but again the liquid volume in the capillary was lower than 1% of the overall liquid volume in the system.

Table 2
Average rates (g m^{-3}_{gas} h^{-1}) obtained during the methane biodegradation experiments in the system.

Condition	rCH_4	rCO_2	rO_2
1	−1.6 ± 0.0	3.5 ± 0.6	−6.3 ± 0.8
2	−1.2 ± 0.0	2.3 ± 0.4	−4.2 ± 0.7
3	−1.9 ± 0.1	3.8 ± 0.3	−7.5 ± 0.5
4	−1.6 ± 0.0	3.6 ± 0.0	−6.6 ± 0.1
5	−1.7 ± 0.1	5.1 ± 0.2	−8.2 ± 0.4
6	−2.0 ± 0.0	5.9 ± 0.2	−9.7 ± 0.2
7	−2.8 ± 0.2	6.4 ± 0.1	−12.5 ± 0.9

$-rCH_{4cap}$ was estimated from Eq. (4) between 36.7 and 77.3 g $m^{-3}_{reactor}$ h^{-1} (Fig. 5), the highest value (without transfer vector) was superior than that obtained by Rocha-Rios et al. [8] in a stirred tank reactor operated at 800 rpm and added with 10% (v/v) of silicone oil, where the highest methane removal rate reached was only 50.7 g $m^{-3}_{reactor}$ h^{-1} but with higher power consumption and higher biomass concentration (3 g L^{-1}).

Throughout the experiment a considerable amount of cells grew attached to the wall of the gas–liquid separator whereas fewer grew on the capillary's wall. These adhered bacteria were not circulating with the liquid and they must have contributed importantly to methane removal in the gas–liquid separator.

3.3.1. Taylor flow effect on methane oxidation

As shown in Fig. 5 and Table 2, the Taylor flow presence in the system (conditions 1, 3 and 6) always increased the methane removal with respect to the control system without Taylor flow (introducing gas and liquid independently to the separator) represented by conditions 2, 4 and 5. This confirmed the effect of Taylor flow to increase the mass transfer of poorly soluble compounds as methane or oxygen in the system.

3.3.1.1. Gas–liquid separator. Tripling the gas flow (from 50 to 150 mL min^{-1}) resulted in a methane removal improvement of 33% in the gas–liquid separator (conditions 2 and 4, respectively).

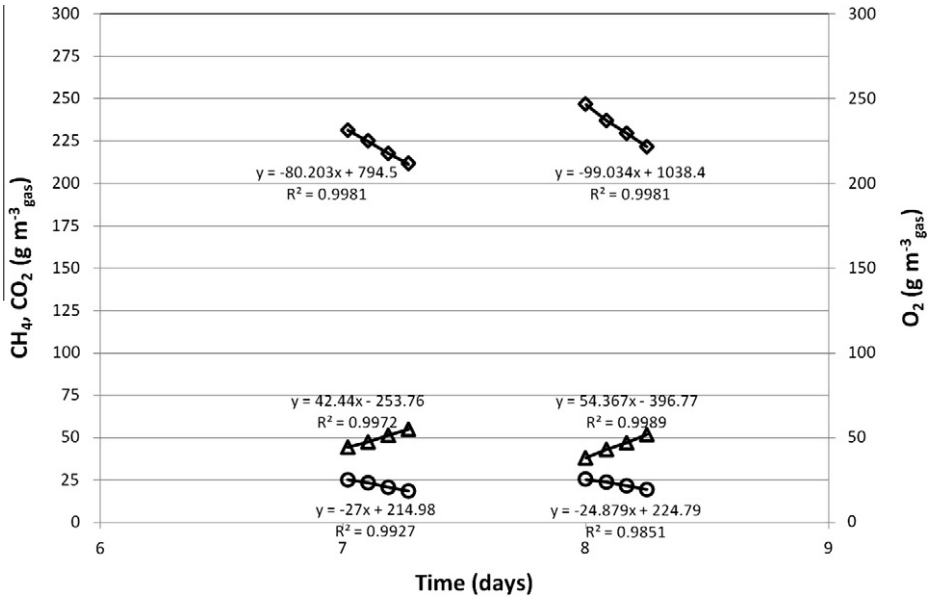

Fig. 4. Time course of CH_4 (-○-), O_2 (-◇-) and CO_2 (-Δ-) concentrations before and after of doubling the biomass concentration in the system. The slopes of the linear fit represent the consumption (CH_4, O_2), or production rates (CO_2).

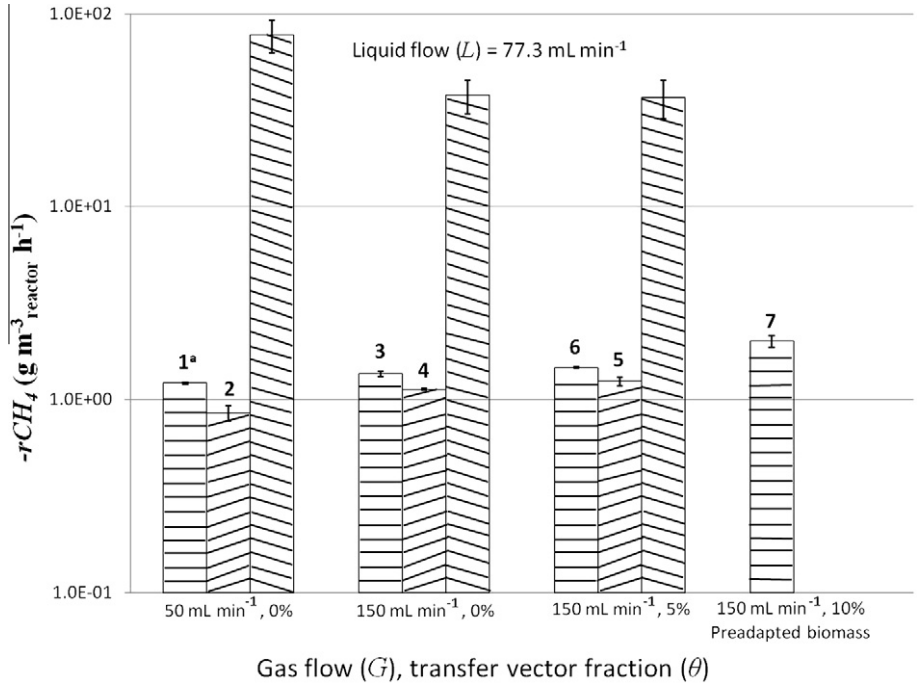

Fig. 5. Methane removal rates in the overall system (⊟), gas–liquid separator (◪) and capillary (◹) for two Taylor flows and two S100 fractions by the sulfite method. [a]Numbers represent the experimental condition tested in Tables 1 and 2.

The huge impact of the gas flow increase on methane biodegradation in the separator can be explained considering the high area of the liquid exposed to the gas flow (superficial aeration) in this recipe.

3.3.1.2. Capillary channel. Although the gas flow increase resulted in small improvements of k_La in the capillary channel during the mass transfer experiments, a reduction of 51% in methane removal rate was estimated in this channel by tripling the gas flow from 50 to 150 mL min^{-1} (Fig. 5 and Table 2). This behavior could be explained considering the reduction in the capillary liquid volume where bacteria were suspended at increasing the gas flow (higher gas holdup in the channel). Estimations of the average methane removal rate per volume of liquid in the capillary were 1.1×10^{-3} and 7.1×10^{-4} g m_{liq}^{-3} h^{-1} for gas flows of 50 and 150 mL min^{-1}, respectively.

3.3.1.3. Overall system. As a consequence of the Taylor flow presence in the capillary channel, the methane oxidation rates in the overall system (conditions 1 and 3) were 43% and 20% higher than those obtained in the gas–liquid separator (conditions 2 and 4), respectively. It seems clear that main contribution of capillary channel in the bioreactor was increasing the methane transfer to the liquid, which was then consumed in the gas–liquid separator as can be deduced considering that k_La was increased in the capillary channel during the abiotic mass transfer experiments while $-rCH_4$ was reduced in this channel during the biodegradation experiments.

The contributions of separator and capillary to the overall methane removal rate were 70% and 30% respectively, at the lowest gas flow, with 83% and 17% at the highest. Therefore, the main impact of increasing the gas flow on mass transfer and consequently on methane oxidation was located in the gas–liquid separator which occupied approximately 99.1% of the total liquid volume in the system. The balance between methane removal reduction in the capillary and improvement in the gas–liquid separator produced an overall improvement in the oxidation rate of 12% by increasing the gas flow in the bioreactor.

3.3.2. S100 addition effect on methane oxidation

The addition of S100 (5% v/v) maintaining constant the gas flow (150 mL min^{-1}) was reflected in additional increases on methane oxidation of 8% in the overall system and 10% in the gas–liquid separator (conditions 6 and 5 respectively), while no increase was determined in the capillary.

The abiotic mass transfer experiments showed that group k_La decreased in the capillary but increased in the separator with S100 addition. The biodegradation rate scales as $r \sim k_La C^*$, where C^* is the solubility. Therefore, we interpret the small increase of overall performance in the oxidation rate as a consequence of positive effects on k_La and C^* in the gas–liquid separator only.

Finally, when the methanotrophic community was replaced by biomass from the same source but growing previously in nutrient medium with 10% (v/v) of S100 (during 2 months) (condition 7), the methane biodegradation in the overall system was 27% higher than the corresponding value determined to 5% (condition 6). It is possible that preadapted biomass could stabilize the emulsion producing biosurfactants and/or bioemulsifiers which reduced the oil drops diameter and promoted a possible uptake of substrates directly from the organic phase as proposed by MacLeod and Daugulis [13].

The main methane removal in the system through the experiment was always localized in the gas–liquid separator (70–84%). Nevertheless, the methane removal estimated in the capillary (30–16%) is very important considering that the liquid volume in the capillary was lower than 1% of the global liquid volume in the system, and where the rest was occupied by the separator. The high reproducibility of the kinetics obtained over two different days (Fig. 4) including the addition of a biomass pulse duplicating the cell's concentration without an increase in methane removal indicated that system was always limited by mass transfer. A maximal enhancement on methane biodegradation rate of 135% was observed in the experiment, corresponding to the value obtained in the overall system with 10% of S100 at the highest gas flow (condition 7 using preadapted biomass) with respect to that obtained in the gas–liquid separator without S100 at the minimal gas flow (condition 2).

In a general way, a reduction in the bubbles size was observed with the S100 addition in the capillary (data not shown). During

the abiotic experiments the S100 oil drops were well dispersed in the water slugs; however, during the methane removal experiments the S100 oil drops were not observed by the naked eye, possibly due to biosurfactants production by cells stabilizing the emulsion. Moreover, it should be emphasized that the cells adhered in the separator's wall throughout the experiment could contribute to the overall methane removal in the system, consuming methane directly from the gas phase.

Estimations between one and two orders of magnitude higher were determined in volumetric mass transfer coefficient (k_La) and volumetric removal rate of methane (rCH_4) using a segmented gas–liquid flow through a capillary channel with respect to those obtained in the gas–liquid separator acting as a stirred tank with superficial aeration. These increases are similar compared to values reported for turbulent (airlift and stirred tank bioreactors) and laminar contactors (biotrickling filters). Moreover, the experimental results are consistent with the order of magnitude analysis realized by Kreutzer et al. [21].

Therefore, the capillary bioreactor is a promising strategy to increase the removal of poorly water soluble compounds in air treatment applications with decreased power consumptions. These systems can be an alternative to the so-called two-phase partition bioreactors (TPPBs) avoiding the use of an organic phase, which increases costs and may affect the hydrodynamics of the system by a higher viscosity and emulsification.

4. Conclusions

It was demonstrated that Taylor flow presence in a capillary bioreactor permits obtaining k_La values at least an order of magnitude higher than typical stirred tank reactors and other turbulent (airlift, bubble columns) and laminar (biofilter, biotrickling filter) contactors. Contrary to the turbulent contactors, the addition of an organic phase impacts negatively the mass transfer in the capillary, likely due to an increased liquid viscosity (emulsion). Therefore, capillary bioreactors form a promising technology for biological gas treatment of hydrophobic compounds. The highest specific methane removal rate obtained in this study (1.5×10^{-2} $gCH_4\ g_{biomass}\ h^{-1}$) with 10% (v/v) of S100 was slightly lower than that obtained previously in a stirred tank (1.7×10^{-3} $gCH_4\ g_{biomass}\ h^{-1}$) at 800 rpm [8], but with one order of magnitude lower power consumption. Additional experiments are required to determine the behavior of the system at longer operation times and the scaling-up of the capillary channel to a monolithic n-channels package.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2012.11.065.

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