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Abstract: The present study aimed at maximizing the performance of a standard biotrickling filter (BTF) devoted to the treatment of CH4 at low concentrations by enhancing the mass transfer using optimum liquid recycling rates and an innovative gas recycling strategy. Internal gas recycling favored CH4 abatement in the early stages of BTF operation and supported stable elimination capacities (ECs) above 30 g m-3 h-1 at an empty bed residence time of 4 min and a liquid recycling velocity of 5 m h-1, which represented the highest ECs achieved in single phase BTFs to date. A comprehensive energy analysis confirmed that internal gas recycling could increase CH4 abatement by 50% at only 10% higher operating costs. The BTF exhibited a high microbial diversity (Shannon-Wiener indices of 2.5-2.8) dominated by Type I methanothrophs, likely due to the presence of high Cu2+ concentrations. Mass transfer limitations from the aqueous phase to the microorganisms, attributed to biomass accumulation in the packing material, were identified under the long term operation.

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Cover Letter

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Marc Deshusses
Chemical Engineering Journal
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Dear Professor Deshusses,

Please find enclosed our unpublished original manuscript "**Methane abatement in a gas-recycling biotrickling filter: evaluating innovative operational strategies to overcome mass transfer limitations**" co-authored by José M. Estrada, Raquel Lebrero, Guillermo Quijano, Rebeca Pérez, Ivonne Figueroa, Pedro A. García-Encina, and Raúl Muñoz. All authors are aware of the CEJ ethics policy, declare no conflict of interest and accept the responsibility for the present manuscript. This manuscript has been prepared according to the CEJ guide for authors.

The increased public awareness of environmental problems and the urgent need to reduce anthropogenic GHG emissions worldwide are promoting an intensive research on the development of cost-effective and environmentally friendly CH_4 abatement technologies. The present study aimed at maximizing the abatement capacity of a standard, single-phase BTF treating dilute CH_4 emissions using an innovative internal gas recycling strategy to overcome previously reported gas-liquid mass transfer limitations. The BTF achieved high CH_4 elimination capacities and unexpected liquid-biofilm mass transfer limitations associated to biomass overgrowth were identified.

In order to avoid any potential conflict of interests based on the current good relationships between Spanish groups working in the field of biofiltration, the authors would highly appreciate the absence of Spanish researchers/academics in the peer-review of this work.

Based on the recent and increasing relevance of anthropogenic GHG emissions and their implications on climate change, we strongly believe that this paper fits well in the scope of *Chemical Engineering Journal* and will certainly attract international attention.

We look forward to your evaluation.
Best regards,

Raúl Muñoz **José M. Estrada**

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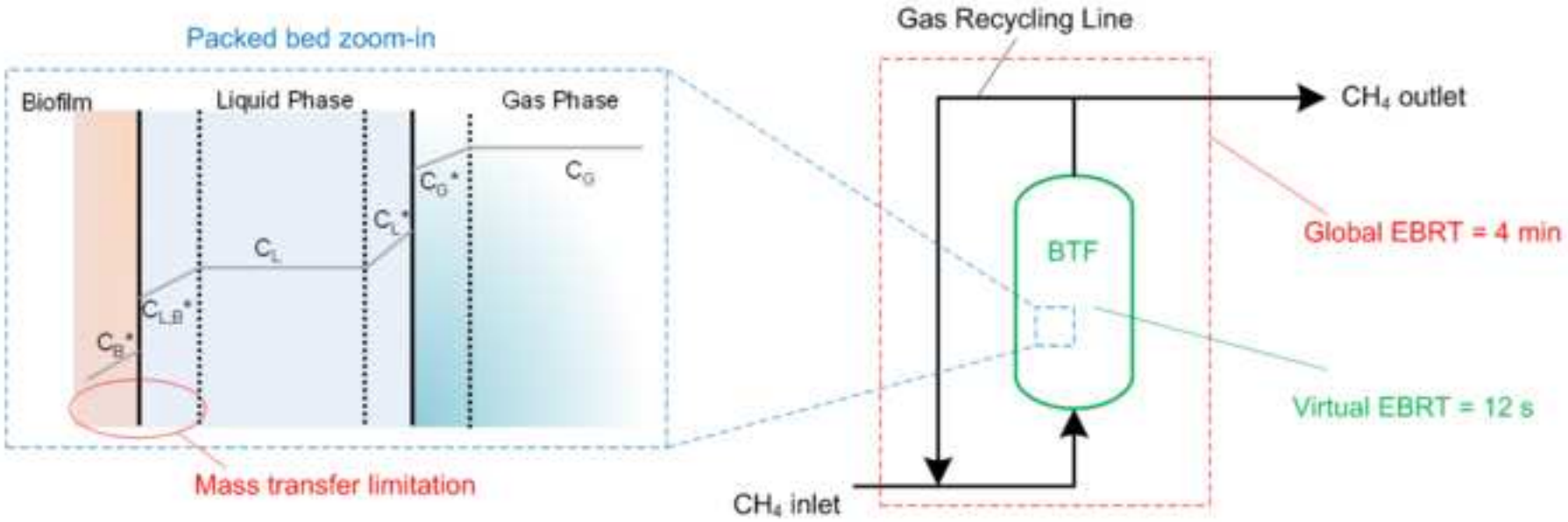
Graphical Abstract (for review)



***Highlights (for review)**

- Internal gas recycling in a BTF was successful at enhancing CH_4 removal.
- Stable CH_4 elimination capacities above 30 g m^{-3} h^{-1} were obtained.
- Type I methanotrophs were dominant in the highly diverse community in the BTF.
- The BTF faced non gas-liquid mass transfer limitations due to biomass overgrowth.

Methane abatement in a gas-recycling biotrickling filter: evaluating innovative operational strategies to overcome mass transfer limitations

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Abstract

The present study aimed at maximizing the performance of a standard biotrickling filter (BTF) devoted to the treatment of CH_4 at low concentrations by enhancing the mass transfer using optimum liquid recycling rates and an innovative gas recycling strategy. Internal gas recycling favored CH_4 abatement in the early stages of BTF operation and supported stable elimination capacities (ECs) above 30 g m^{-3} h^{-1} at an empty bed residence time of 4 min and a liquid recycling velocity of 5 m h^{-1}, which represented the highest ECs achieved in single phase BTFs to date. A comprehensive energy analysis confirmed that internal gas recycling could increase CH_4 abatement by 50% at only 10% higher operating costs. The BTF exhibited a high microbial diversity (Shannon-Wiener indices of 2.5-2.8) dominated by Type I methanothrophs, likely due to the presence of high Cu^{2+} concentrations. Mass transfer limitations from the aqueous phase to the microorganisms, attributed to biomass accumulation in the packing material, were identified under the long term operation.

Keywords: biotrickling filter, greenhouse gas, mass transfer, methane, polyurethane foam.

1.Introduction

Methane, with a global warming potential 20 times higher than that of CO_2, is nowadays the second most relevant greenhouse gas (GHG) emitted to the atmosphere. Atmospheric CH_4 concentrations in 2011 exceeded pre-industrial levels by 150% [1, 2], with anthropogenic emissions representing 50-65 % of the total CH_4emission inventory worldwide [1]. In this context, the increased public awareness of environmental problems and the urgent need to reduce anthropogenic GHG emissions worldwide are promoting an intensive research on the development of cost-effective and environmentally friendly CH_4 abatement technologies.

Methane emissions not suitable for energy recovery (methane content < 30%) have been traditionally treated using flaring or incineration as end-of-the-pipe technologies [3]. Unfortunately, while these oxidation technologies are only cost-effective for emissions containing CH_4 concentrations over 20%, more than 50% of the anthropogenic CH_4 is emitted at concentrations below 3% [4]. Dilute CH_4 emissions are typically found in old landfills fugitive emissions or gas recovery systems (0-20%), in ventilated coal mines (0.1 – 1 %) or in covered liquid manure storage tanks (0-3%) [5-9]. In this regard, biological technologies represent a promising end-of-the-pipe solution for the treatment of dilute off-gas emissions, biotrickling filtration being one of the most cost-effective configurations due to its robustness and low operating costs [10, 11].

However, pollutant mass transfer limitations often reduce the abatement potential and hinder the full-scale application of biotrickling filters (BTFs) devoted to the treatment of highly hydrophobic compounds such as CH_4[12]. Most recent research studies have focused on CH_4 mass transfer enhancement by either applying complex bioreactor

configurations such as horizontal biofilm, airlift or tailor flow reactors [13-15] or by adding non-aqueous phases and surfactants to conventional bioreactor configurations [4, 16]. However, both approaches have resulted in limited elimination capacities and entailed high operating costs [16]. Therefore, the development of simple and cost-effective bioreactor configurations and operational strategies devoted to CH_4 abatement will be crucial in the global fight against climate change.

The present study aimed at maximizing the abatement capacity of a standard, single-phase BTF treating dilute CH_4 emissions. First, the influence of the gas empty bed residence time (EBRT) and the linear liquid recycling velocity (U_L) on the abiotic k_La_{CH4} and pressure drop in the BTF was characterized. Secondly, the influence of U_L, internal gas recycling and liquid media renewal rate on the CH_4 biodegradation performance of the BTF was evaluated. Internal gas recycling constitutes an innovative mass transfer enhancement approach based on the decoupling of the gas-liquid turbulence inside the reactor from the actual gas residence time. Finally, the dynamics of the microbial community structure responsible for CH_4 biodegradation were elucidated.

2. Materials and Methods

2.1 Chemicals

The mineral salt medium (MSM) used during the experimentation was a modified Brunner medium consisting of (gL^{-1}): $Na_2HPO_4{\cdot}12H_2O$, 6.15; KH_2PO_4, 1.52; $NaNO_3$, 0.61 (used instead of $(NH_4)_2SO_4$to prevent the inhibition of methanotrophs by ammonia [17]); $MgSO_4{\cdot}7H_2O$, 0.2; $CaCl_2{\cdot}2H_2O$, 0.05; EDTA, 0.005; $FeSO_4{\cdot}\ 7H_2O$, 0.002; H_3BO_3, 0.0003; $CoCl_2{\cdot}\ 6H_2O$, 0.0002; $ZnSO_4{\cdot}7H_2O$, 0.0001; $Na_2Mo_4{\cdot}2H_2O$, 0.00003;

$MnCl_2 \cdot 4H_2O$, 0.00003; $NiCl_2 \cdot 6H_2O$, 0.00002; $CuCl_2 \cdot 2H_2O$, 0.00001. Cu^{2+} was supplemented to the MSM from a 10 g L^{-1} $CuSO_4$ stock solution to the target concentrations in order to avoid copper limitations. All chemicals were purchased from Panreac (Spain) with a purity higher than 99.0%. Methane (99.5% purity) and nitrogen (99.9% Purity) were supplied by Abello-Linde, S.A. (Spain), while silicone oil 200 cSt (99.9% purity) was purchased from Sigma Aldrich (USA).

2.2 Inoculum

The BTF was inoculated with methanotrophic cultures enriched from aerobic activated sludge from Valladolid wastewater treatment plant (Valladolid, Spain). Sludge samples were acclimated separately to CH_4 degradation for 37 days at Cu^{2+}concentrations of 5, 10, 25 and 50 μM in order to assess the influence of copper concentration on methane biodegradation. Methanotrophic cultures were enriched at 25 ºC in 1250 mL bottles containing 500 mL MSM and batchwise fed (8 amendments) with CH_4 at initial headspace concentrations of ≈ 14 g m^{-3}. Based on the negligible influence of Cu^{2+} concentration on the CH_4 biodegradation rate (data not shown), the BTF was inoculated with 300 mL of each culture and further operated at 10 μM Cu^{2+}.

2.3 Experimental set-up

A laboratory scale BTF consisting of a cylindrical jacketed PVC column (0.08 m inner diameter) was packed with polyurethane foam (PUF) to a working packed bed volume of 4 L. The packing material consisted of 1 cm^3 PUF cubes (Filtren TM 25280, Recticel Iberica S.L.) with a net density of 20–24 kg m^{-3} and a specific surface area of 1000 m^2 m^{-3}. MSM (1.2 ± 0.2 L) was continuously recycled into the BTF from an external 1.2 L

jacketed holding tank stirred at 700 rpm (Agimatic-S, Selecta®, Spain) (Figure 1). All experiments were carried out at 20ºC.

2.4 Influence of the EBRT and liquid recycling on k_La_{CH4} and pressure drop

The overall volumetric mass transfer coefficients for O_2 were determined at EBRTs of 12, 60, 120, and 240 s and liquid recycling velocities (U_L) of 0.6, 2, 3, 4, and 5 m h^{-1} using distilled water as the recycling liquid. N_2 was initially supplied to the BTF until the O_2 concentration in the liquid phase (recorded in the holding tank) reached ≈0 ppm. Then, air was supplied to the BTF while monitoring the increase in dissolved oxygen concentration. The experimental data were fitted to the model described by Lebrero et al. (2012) [18]. The overall k_La values for CH_4were estimated from k_La_{O2}using the correlation reported by Yu et al. 2006 (Equation 1) [19]:

$$\frac{k_L a_{CH4}}{k_L a_{O2}} = \frac{\left(1/V_{m,CH4}\right)^{0.4}}{\left(1/V_{m,O2}\right)^{0.4}} \qquad \text{Equation 1}$$

where the mass transfer coefficient of a target gas pollutant (k_La_{CH4}) can be estimated from the coefficient of a reference gas (k_La_{O2} in the present study) previously determined in the same reactor under the same operating conditions by means of the molar volumes of the gaseous compounds ($V_{m,X}$).

The pressure drop across the packed bed was also recorded under all the EBRTs and U_L tested. Tests in the un-packed BTF were also carried out at all conditions assessed in order to account exclusively for the pressure drop caused by the packed bed.

2.5 Optimization of CH_4 biodegradation in the BTF

The synthetic methane-polluted emission fed to the BTF (15.3±0.5 g CH_4 m^{-3}, 2.2±0.1 %) was obtained by mixing a pure methane stream with a pre-humidified air stream in a

mixing chamber. The emission flow-rate and CH_4 concentrations were regulated by means of mass flow controllers (Aalborg, USA), resulting in an EBRT of 4 min and an overall loading rate of 229±8 g m^{-3} h^{-1}. The internal gas recycling was carried out using an EVO 10 compressor (Electro A.D. S.L., Spain) by re-pumping 18 L min^{-1} from the top to the bottom of the BTF and mixing this recycled air flow with the fresh methane-polluted emission (Figure 1). This innovative operational mode allowed the BTF to operate with a global EBRT of 4 min and the gas-liquid turbulence at an effective EBRT of 12.6 s.

The MSM renewal rate was set at 50 mL day^{-1} (dilution rate, D =0.045 d^{-1}) from days 0 to 47, 100 mL d^{-1} (D=0.09d^{-1}) from days 48 to 66, and 300 mL day^{-1} (D=0.27d^{-1}) from days 67 to 110 in order to avoid both nutrient limitation and the accumulation of toxic inhibitory metabolites in the recycling liquid. The liquid recycling rates tested in the BTF (200, 500, and 1500 mL min^{-1} corresponding to U_L of 2.3, 5, and 15 m h^{-1}) were controlled by means of a Dosapro series G™ A pump (Milton Roy Ltd., USA) and a 520-S pump (Watson Marlow, UK)at the highest flow rate.

Gas samples were periodically drawn from the sampling ports located at the inlet and outlet of the BTF to monitor the CH_4 and CO_2 concentrations. Liquid samples were periodically drawn from the stirred tank and filtered through 0.45 μm Millipore filters for the determination of pH, total organic carbon (TOC) and total nitrogen (TN) concentrations. Bed compaction was directly measured from the variations in the packed bed height in the BTF. The humidity of the inlet CH_4-laden air stream was measured on-line by a thermohygrometer (Testo 605-H1, Testo AG, Germany) and ranged from 40 to 60%. Water losses by evaporation in the system were balanced by addition of distilled water to keep a constant recycling liquid volume.

2.6 Analytical methods

The CO_2 and CH_4 gas concentrations were determined in a Bruker 430 gas chromatograph (Palo Alto, USA) coupled with a thermal conductivity detector and equipped with a CP-Molsieve 5A (15m × 0.53 μm × 15 μm) and a CP-PoraBOND Q (25m × 0.53 μm × 10 μm) columns. The oven, injector and detector temperatures were maintained at 45 °C, 150 °C and 175 °C, respectively. Helium was used as the carrier and make up gas at 6 mL $min^{-1}$and 24 mL min^{-1}, respectively. The pH was determined using a pH-meter Basic 20 (Crison, Spain), while the concentrations of TOC and TN were measured using a Shimadzu TOC-VCSH analyzer (Japan) equipped with a TNM-1 chemiluminescence module. Dissolved O_2 concentration in the holding tank was measured by means of an oxygen probe (Consort©, Belgium) connected to a multi-parameter analyzer C3020 (Consort©, Belgium) and a computer data logger as described elsewhere [20]. Pressure drop was measured by means of a U-Tube manometer connected to the inlet and outlet of the reactor using water as the manometric fluid.

2.7 Microbiological procedures

Biomass samples from the cultures acclimated at different Cu^{2+} concentrations (5, 10, 25 and 50 μM corresponding to samples A, B, C and D, respectively), from the mixed BTF inoculum (sample E) and from the BTF at days 38 (sample F) and 104 (sample G) were collected and stored at -20ºC in order to evaluate the richness and composition of the bacterial communities. The genomic DNA was extracted according to Lebrero et al. (2011) [23] . The PCR mixture (50 μL) was composed of 25 μL of BIOMIX ready-to-use 2× reaction mix (Bioline, Ecogen) containing reaction buffer, magnesium chloride, deoxynucleotide triphosphates (dNTPs), Taq polymerase and additives, 1 or 2 μL of the extracted DNA, PCR primers 968-F-GC and 1401-R (10μM) (Sigma- Aldrich, St.

Louis, MO, USA) for bacterial 16S rRNA gene amplification, and Milli-Q water up to a final volume of 50 µL. The PCR thermo-cycling program used was previously described in Lebrero et al. (2011). The DGGE analysis of the amplicons was performed with a D-Code Universal Mutation Detection System (Bio Rad Laboratories) using 8% (w/v) polyacrylamide gel with a urea/formamide denaturing gradient from 45 to 65%. The DGGE running conditions were applied according to Roest et al. (2005) [21]. The gels were stained with GelRed Nucleic Acid Gel Stain (biotium) for 1 h and the obtained DGGE patterns processed using the GelCompar IITM software (Applied Maths BVBA, Sint-Martens-Latem, Belgium). After image normalization, bands were defined for each sample using the band search algorithm within the program. Similarity indices of the compared profiles were calculated from the densitometric curves of the scanned DGGE profiles by using the Pearson product–moment correlation coefficient [22]. The peak heights in the densitometric curves were also used to determine the Shannon–Wiener diversity index (H).

The most relevant bands were excised from the DGGE gel in order to identify the bacteria present in the samples above described. The procedure was previously described in Lebrero et al. (2011) [23]. The taxonomic position of the sequenced DGGE bands was obtained using the RDP classifier tool (50% confidence level) [24]. The closest matches to each band were obtained using the BLAST search tool at the NCBI (National Centre for Biotechnology Information) [25]. Sequences were deposited in GenBank Data Library under accession numbers KJ002507- KJ002532.

3. Results and Discussion

3.1 Influence of the EBRT and liquid recycling on k_La_{CH4} and pressure drop

The overall k_La_{CH4} values increased when increasing the liquid recycling velocity and decreasing the EBRT, with a maximum of 280±15 h^{-1} recorded at 5 m h^{-1} and 12 s (Figure 2A). CH_4 mass transfer exhibited a low sensitivity towards variations in the gas EBRT at low liquid recycling velocities. For instance, the overall k_La_{CH4} increased from 37 to 85 h^{-1} (130%) when decreasing the EBRT from 240 to 12 s at a U_L of 0.6 m h^{-1}, while this increase accounted for 220% at a U_L of 5 m h^{-1}. These empirical findings were in agreement with the data reported by Kim and Deshusses (2008), where the volumetric mass transfer coefficient in the liquid film (k_La_w) for $CO_2$was not sensitive to variations in the gas flow-rate at the lowest U_L tested (0.1 m h^{-1}) [26]. This also suggested that the process was limited by mass transfer in the liquid side under low U_L, since only a moderate mass transfer improvement was observed when increasing the turbulence in the gas side. An increasing influence of the EBRT on the overall k_La_{CH4} was recorded at higher U_L (3, 4, and 5 m h^{-1}) likely due to a decrease in the mass transfer resistance in the liquid film (as a result of the higher liquid turbulence), concomitant with an enhanced transport in the gas side. Similarly, a reduced k_La_{CH4} sensitivity towards variations in U_L was recorded at high EBRTs. Therefore, these results suggest that attempts to overcome mass transfer limitations in BTFs by increasing the liquid recycling rate might be only cost-effective at low EBRTs. Internal gas-recycling can help reducing the mass transfer resistances while operating at high EBRTs, which can eventually boost CH_4 abatement in BTFs [13].

On the other hand, no significant influence of the EBRT and liquid recycling velocity on the pressure drop across the packed bed was recorded, with a maximum pressure drop variation from 0.1 to 0.3 Pa m^{-1}_{bed} under the conditions tested (Figure 2B). This finding was of key relevance for the implementation of internal gas-recycling strategies, since any additional energy requirement in this innovative operational mode would

derive from the higher circulating flow rates rather than from an additional pressure drop mediated by the internal gas recycling.

3.2 Optimization of CH_4 biodegradation in the BTF

When the BTF was operated at an EBRT of 4 min and U_L = 2.3 m h^{-1}, the EC remained below 2 g m^3 $h^{-1}$with stable CO_2 production rates of ≈10 g m^{-3} h^{-1} (Figure 3). The high CO_2 production, above the expected levels according to the low CH_4 EC recorded, was attributed to the inoculum endogenous respiration. Then, U_L was increased to 5 m h^{-1} by day 13 in order to overcome possible mass transfer limitations in the system. This change in operational conditions corresponded to an overall abiotic k_La_{CH4} increase from 28 h^{-1} to 88 $h^{-1}$and resulted in fluctuating ECs (4.2 to 16.3 g m^{-3} h^{-1}) from day 14 to 31, which confirmed the occurrence of mass transfer limitation in the liquid side during the previous operational stage. CO_2 production rates gradually decreased in this period, which was attributed to the increasing contribution of anabolism (biomass growth) to CH_4 biodegradation compared to process start-up where endogenous respiration was the predominant process (Figure 3B). This fact was confirmed by visual observation of the significant biomass growth on the packing material and the low CH_4 mineralization observed in this period (24±12%).

Internal gas recirculation was implemented on day 31 at a rate of 18 L min^{-1}, resulting in a virtual EBRT of 12 s in the packing material while maintaining a global EBRT of 4 min and a CH_4 loading rate of 229±8 g m^{-3} h^{-1}. This strategy was expected to increase the mass transfer coefficient for CH_4 by a factor of 3, which agreed with the EC of up to 29 g m^{-3} h^{-1} recorded by day 32 (2.5 fold EC increase). This fact confirmed the potential of internal gas recirculation to enhance CH_4 mass transfer from the gas to the liquid phase. However, a sharp decrease in the EC to 0 g m^{-3} h^{-1} by day 35 was observed,

which was attributed to nutrient limitation in the system. Thus, 500 mL of recycling cultivation broth were replaced by fresh MSM at day 38, which allowed to recover an EC of 27 g m^{-3} h^{-1} on day 39. The EC was then allowed to gradually decrease again in order to confirm a potential nutrient limitation. The absence of CH_4 biodegradation recorded by day 42 coincided with negligible TN concentrations in the recycling liquid medium. Hence, NO_3^-concentrations in the BTF were daily restored from days 43 to 47 by adding 12 mL of a 100 g L^{-1} stock nitrate solution, which entailed TN concentrations of 72 ± 32 mg $L^{-1}$and steady EC of 21.7 g m^{-3} h^{-1} by day 48. Therefore, nitrogen was identified as the key limiting factor under internal gas recycling at 18 L min^{-1} and U_L of 5 m h^{-1}, and an increase in the MSM renewal to a D of 0.09 $day^{-1}$was implemented. This higher frequency in MSM exchange was able to maintain ECs of 18.5 ± 3.0 g m^{-3} h^{-1} for only 7 days. CH_4 biodegradation performance started to decrease again by day 55 likely due to the accumulation of inhibitory biodegradation metabolites. Hence, while a D of 0.09 day^{-1} was able to maintain TN concentrations at 149 ± 28 mg L^{-1}, TOC concentration in the recycling liquid increased from 77 to 161 mg L^{-1} from day 55 to day 66. The present empirical findings were in agreement with the deterioration in CH_4 oxidation activity observed by Mancebo et al. (2012) in an organic packing-based biofilter at high dissolved organic carbon concentrations [27]. Therefore, a new MSM dilution rate of 0.27 $day^{-1}$was implemented from day 66 onward, which allowed to maintain TOC concentrations at ≈ 100mg L^{-1} and TN concentrations >100 mg L^{-1}. In this context, the EC gradually recovered to steady values of 22.2 ± 1.8 g m^{-3} h^{-1} from day 72 to 82 concomitant with a rise in CO_2 production up to 47.3 ± 4.1 g m^{-3} h^{-1} (89% CH_4 mineralization).

Internal gas recirculation was stopped at day 82 in order to confirm the potential of this operational strategy to enhance CH_4 mass transport in the BTF operating at the real

EBRT of 4 min. Surprisingly, no deterioration in CH_4 biodegradation was observed following the interruption of the gas recirculation, with average ECs and CO_2 production rates of 22.2 ± 2.4 g m^{-3} h^{-1} and 51.9 ± 2.3 g m^{-3} h^{-1}, respectively, from day 82 to day 94. Based on the previous abiotic mass transfer characterization, k_La_{CH4} decreased from 280 to 88 h^{-1} when the EBRT increased from 12 s to 4 min. It can be hypothesized that biomass growth in the packed bed modified both the hydrodynamics and mass transfer processes in the BTF. Popat and Deshusses (2010) recently reported the complex and significant influence of biomass growth on mass transfer mechanisms in BTFs, where shifts in rate-governing steps were associated to a biomass-mediated modification of the interfacial area available for pollutant mass transfer [28]. Likewise, Arellano-García et al. (2013) demonstrated that the accumulation of biomass can modify the hydrodynamics of the recycling liquid from plug flow, affecting pollutant biodegradation in the BTF [29].

The influence of U_L on the EC in the absence of internal gas recirculation was further assessed by increasing the liquid recycling rate from 5 to 15 m h^{-1} on day 94. Despite an increase in mass transfer was expected from the extrapolation of the results presented in Figure 2A, the reactor maintained stable ECs of 22.5 ± 1.7 g m^{-3} h^{-1} from days 94 to 110 showing a slight increase in the CO_2 production rates with an average value of 54.2 ± 5.4 g m^{-3} h^{-1} (Figure 3). A mass transfer limitation test was carried out on day 97 in order to elucidate the rate-limiting step by increasing the inlet gas CH_4 concentration from 15 to 41 g m^{-3} for 3.5 h (2.8 fold increase) (Figure 4). The EC rapidly increased from 24.3 to 63.8 g m^{-3} h^{-1} (2.6 times increase) during this step CH_4 load increase, and concomitantly decreased to previous steady state values of 19 g m^{-3} h^{-1} when the inlet CH_4 concentration was decreased to 15 g m^{-3}. This test confirmed that CH_4 abatement in the BTF was mass transfer limited, ruling out a potential biological limitation [30]. In

addition, the determination of CH_4 concentration in the liquid phase at the bottom of the column by day 100 revealed values of 0.22 ± 0.04 g m^{-3}, which were close to the theoretical equilibrium concentration of 0.40 g m^{-3} calculated by the Henry's law. This confirmed that CH_4 was effectively transferred to the liquid phase but suggested that the diffusive transport through the biofilm was the limiting mass transfer process. In view of the above-mentioned results, the occurrence of a mass transfer limitation between the liquid phase and the biofilm colonizing the packed bed might be hypothesized (Figure 5). This would explain the absence of increase in EC when increasing the gas velocity, and the high CH_4 concentrations recorded in the recycling liquid phase. Therefore, any operational modification to enhance the gas-liquid mass transfer would be unfruitful to increase CH_4 abatement. However, the increase in the U_L was also unsuccessful in enhancing the liquid-biofilm mass transfer, probably due to interfacial area decrease caused by biomass growth [28].

Finally, a significant packed bed compaction was recorded during BTF operation. A 22% bed compaction was recorded by day 87, increasing up to 34% by day 98 and to 35% by day 105. This high bed height decrease determined the effective EBRT and consequently the CH_4 load. Thus, the average ECs reported (≈22g m^{-3} h^{-1}) during the final stages of the experiment (days 94-110) should be corrected to account for the real packed bed volume, resulting in stable real ECs above 30 g m^{-3} h^{-1}[31]. To the best of our knowledge, these ECs were higher than any of the previously reported ECs in the scarce literature available to date for single phase BTFs treating CH_4. For instance, Avalos et al. (2012) found maximum ECs of ≈ 10 g m^{-3} h^{-1} in a stone-based BTF operated at 4.25 min of EBRT and CH_4 loads of 62 g m^{-3} h^{-1}, while Rocha-Rios et al. (2009) reached 22 g m^{-3} h^{-1} in a polyurethane foam-packed BTF operated at 4.8 min of EBRT and CH_4 loads of 140 g m^{-3} h^{-1}[32]. BTFs operated an EBRTs of 4-5 min

support ECs similar to those obtained in full scale biofilters (BFs) operated at EBRTs sometimes exceeding 60 min (20-80 g m^{-3} h^{-1}) [3], while low EBRTs (4.3 min) in BFs often result in lower ECs (e.g. ≈ 19 g m^{-3} h^{-1}) [33].

3.3 Energy considerations during operation with internal gas recycling

A cost-benefit analysis was conducted in order to evaluate the environmental sustainability of this operational strategy under two scenarios based on the overall k_La_{CH4} previously determined. Under reference scenario 1 (U_L = 5 m h^{-1}, EBRT = 240 s, no internal gas recycling) the BTF would require 1 energy unit and remove 1 CH_4 unit (or 20 CO_2 equivalent units) (Table 1). Thus, 20 CO_2 equivalents could be removed per unit of energy applied. The implementation of internal gas recycling to achieve a virtual EBRT of 12 s (by recycling 18 times the inlet flow rate) would increase the k_La_{CH4} by a factor of 3 (Figure 2A), removing 60 CO_2 equivalents. In this particular scenario, the energy consumption associated to gas pumping would increase by a factor of 18 (based on the fact that pressure drop remains constant, Figure 2B), and the efficiency would decrease from 20 to 3.2 units of CO_2 equivalents removed per unit of energy applied. This would result in an increase in the annual operating cost of 260 %, based on the fact that energy consumption in BTFs accounts for 22 % of the total operating costs (Estrada et al. 2012). On the other hand, an increase in the EBRT by a factor of 3 to achieve comparable ECs to those obtained under internal gas recycling would entail an increase in the operating cost of 150% (Estrada et al. 2011, 2012).

Nevertheless, internal gas recycling might be economically and energetically favorable under different operating conditions. The BTF would hypothetically remove 5 CO_2 equivalents under reference scenario 2 (U_L = 2 m h^{-1}, EBRT = 240 s and no internal gas recycling) and 15 CO_2 equivalents when internal gas recycling decreases the virtual

EBRT to 120 s. Under this internal gas recycling, the BTF would double the energy consumption, resulting in removals of 7.5 units of CO_2 equivalent per unit of energy applied compared to 5 in reference scenario 2 (Table 1). In this case, the increase in the annual operating costs under internal gas recycling would account for only 10%, while an increase in the EBRT by a factor of 3 to achieve comparable ECs to those obtained under gas recycling would entail an increase in the operating cost of 150% (Estrada et al. 2011, 2012). However, all these are hypothetical considerations and were not observed in the experimental operation of the BTF probably due to a biomass excessive growth which led to additional mass transfer limitations. Thus, finding optimal biomass content can be of key relevance for further optimization of the gas recycling strategy here proposed.

3.4 Bacterial population dynamics

The structure of the bacterial communities in the inocula and BTF was elucidated by sequencing 21 bands from the DGGE gel (Figure 6). The closest matches for each band, along with its similarity percentage and sources, are shown in Table 2 (Supplementary material). The phylum *Proteobacteria* was predominant in the cultures acclimated to different copper concentration and in the biotrickling filter regardless of the operational stage with 17 bands belonging to this phylum (DGGE bands1 to 7 and 13 to 22, Fig. 6). Most of these *Proteobacteria* were closely related to methane oxidizing bacteria (methanotrophs) and are often found at the anoxic/oxic interface of landfills, wastewater treatment plants, soils, rice paddies, peat bogs, wetlands and sediments[34, 35].

Aerobic methanotrophic bacteria obtain energy via CH_4 to CO_2 oxidation based on their ability to synthesize methane mono-oxygenases [36, 37]. Most methanotrophs belonged to the bacterial phylum Proteobacteria, in the classes Gammaproteobacteria (Type I) and

Alphaproteobacteria (Type II) [38]. Type I methanotrophs, which include genera such as *Methylomonas*, *Methylobacter* and *Methylococcus*, [2] produce particulate methane monooxygenase (pMMO) and possess a more efficient CH_4-oxidizng metabolism than their type II counterparts [11, 35].

Both type I and II methanotrophs were identified in this work, type I being by far the most abundant type of methanotrophs. The closest relatives for DGGE bands 2-18 were type I methanotrophs [2], although the similarity was as low as 84 % for band 2 and 92 % for band 15. The preferential enrichment of type I methanotrophs was likely due to the high Cu^{2+} content (10 µM) in the mineral salt medium, which has been often correlated with the production of pMMO instead of the soluble form of the enzymes MMO [39]. Bands 19 and 20, which were relevant in the BTF but not in the initial inoculum belonged to the *Xanthomonagaceae* family and were related to other liquid or gas pollutant degraders. The DGGE band 21, specifically affiliated to the *Methylocystis* genus, was the only one belonging to type II methanotrophs. Bacteria belonging to the *Methylocystis* genus have been also found in biofilters treating methane [40]. Finally, while the DGGE band 22 was 100% similar to a *Betaproteobacteria* isolated from a petroleum hydrocarbon-contaminatedwater[41], bands 23 to 26 were affiliated with the phylum *Chlamydae, Firmicutes, Gemmatimonadetes and Verrucomicribia,* but their similarity to the closest relatives ranged from 88 to 95%.

The Shannon-Wiener diversity indices for the methanotrophic cultures enriched at different Cu^{2+} concentrations revealed an increase in bacterial diversity at increasing Cu^{2+} concentrations in the cultivation medium (1.8, 2.3, 2.4 and 2.6 at Cu^{+2} concentrations of 5, 10, 25 and 50 µM, respectively). A high bacterial diversity (2.5-2.8) was maintained in the biotrickling filter from inoculation throughout the complete experimental period (Figure 6, samples E, F and G). However, a low similarity was

observed between the inoculum and the community established in the reactor by day 38 (31.8% similarity) or by the end of the experiment (27.4% similarity). A significant evolution (66.4% similarity) of the communities governing CH_4 oxidation in the BTF was also observed from day 38 to 104. These results showed the progressive establishment of bacterial populations with high functional resilience and redundancy capable of maintaining high ECs despite the changes in their structure [42].

4. Conclusions

Internal gas recycling enhanced the performance of the BTF in the early stages of operation, which agreed with the data obtained in the abiotic mass transfer tests. Under certain operating conditions this strategy can theoretically result in a 50% improvement in the BTF energy use efficiency (CH_4 removal per unit of energy applied) at significantly lower operating costs than other strategies such as EBRT increase. However, the reactor faced additional mass transfer limitations not easily overcome by increasing the gas-liquid mass transfer as a result of biomass accumulation in the packed bed. CH_4 mass transfer from the liquid phase to the biofilm was identified as the limiting step during CH_4 abatement in our particular BTF. ECs higher than 30 g m^{-3} h^{-1} were achieved at an EBRT of 4 min and U_L of 5 m h^{-1}, which represent the highest ECs recorded in a single-phase BTF treating CH_4. A high diversity was found in the reactor through the experimental period showing high functional resiliency and redundancy and maintaining high EC despite changes in the bacterial community. Type I methanotrophs were dominant, proving that high Cu^{2+} concentrations in the recycling MSM was a successful strategy to promote their growth.

5. Acknowledgements

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Figure captions

Figure 1. Schematic representation of the experimental set-up. 1. Ambient air compressor, 2. Humidifying column, 3.CH_4 reservoir, 4. Mass flow controllers, 5. Mixing chamber, 6. Gas sampling ports, 7. Stirred tank, 8.Liquid recycling pump, 9.Gas recycling compressor, 10.Liquid sampling port.

Figure 2. Influence of the gas EBRT and liquid recycling velocity (U_L) on k_La for CH_4**(A)**and onthe pressure drop in the packed bed **(B).**

Figure 3. Time course of **(A)** Loading rate (grey line) and EC (white diamonds), and **(B)** CO_2 production rate (black circles) during CH_4 biodegradation in a BTF. Horizontal arrows indicate the MSM exchange rates, while vertical lines indicate the different operational stages: 1. U_L= 2.3 m h^{-1}, 2.U_L = 5 m h^{-1}, 3. Internal gas recycling at 18 L min^{-1}, 4. Gas recycling stopped, 5. U_L = 15 m h^{-1}.

Figure 4. Time course of the EC (white diamonds) and loading rate (black squares) during the mass transfer limitation test.

Figure 5.CH_4 concentration profile representing the mass transfer processes occurring in the BTF and the hypothetical mass transfer resistance governing the process. C_G = bulk concentration in the gas phase, C_G*= Gas phase concentration at the gas-liquid interphase,C_L*= Liquid phase concentration in equilibrium with the gas phase, C_L = bulk concentration in the liquid phase, $C_{L,B}$*= Liquid phase concentration at the liquid-biofilm interphase, C_B*= Biofilm concentration in equilibrium with the liquid phase.

Figure 6. Bacterial DGGE profile of the four cultures acclimated at different Cu^{2+} (A, B, C and D corresponding to 5, 10, 25 and 50 μM, respectively), the mixed microbial inoculum (E), the population present in the BTF at day 38 (F) and 104 (G). The Shannon-Wiener diversity indices are indicated in the upper part of the gel. The sequenced bands are indicated by "▶" and the corresponding number of each band.

Table 1

Table 1. Comparative evaluation of energy consumption and GHG mitigation efficiency of internal gas recycling under two different scenarios. A reference (without gas recycling) and a gas recycle operation mode are considered for each scenario.

		Scenario 1		Scenario 2	
		Ref.	Recycle	Ref	Recycle
Gas recycling ratio (Recycling flow/Feed flow)		0	18	0	1
Conditions	$\mathbf{V_L}$ (m h^{-1})	5	5	2	2
	Virtual EBRT (s)	240	12	240	120
Energy consumed (energy units)		1	19	1	2
CH_4 removed* (CH_4 units)		1	3	0.25	0.75
CO_2 eq. removed (CO_2 units)		20	60	5	15
CO_2 eq. removed / energy consumed		20	3.2	5	7.5
Annual Operating Costs with gas recycling		1	3.6	1	1.1
Annual Operating Costs with EBRT increase**		1	2.5	1	2.5

*Comparative data based on the experimental data from the present study.

**Theoretically calculated by increasing the EBRT of the unit to achieve a similar CH_4 removal to that obtained under internal gas recycling.

Figure 1

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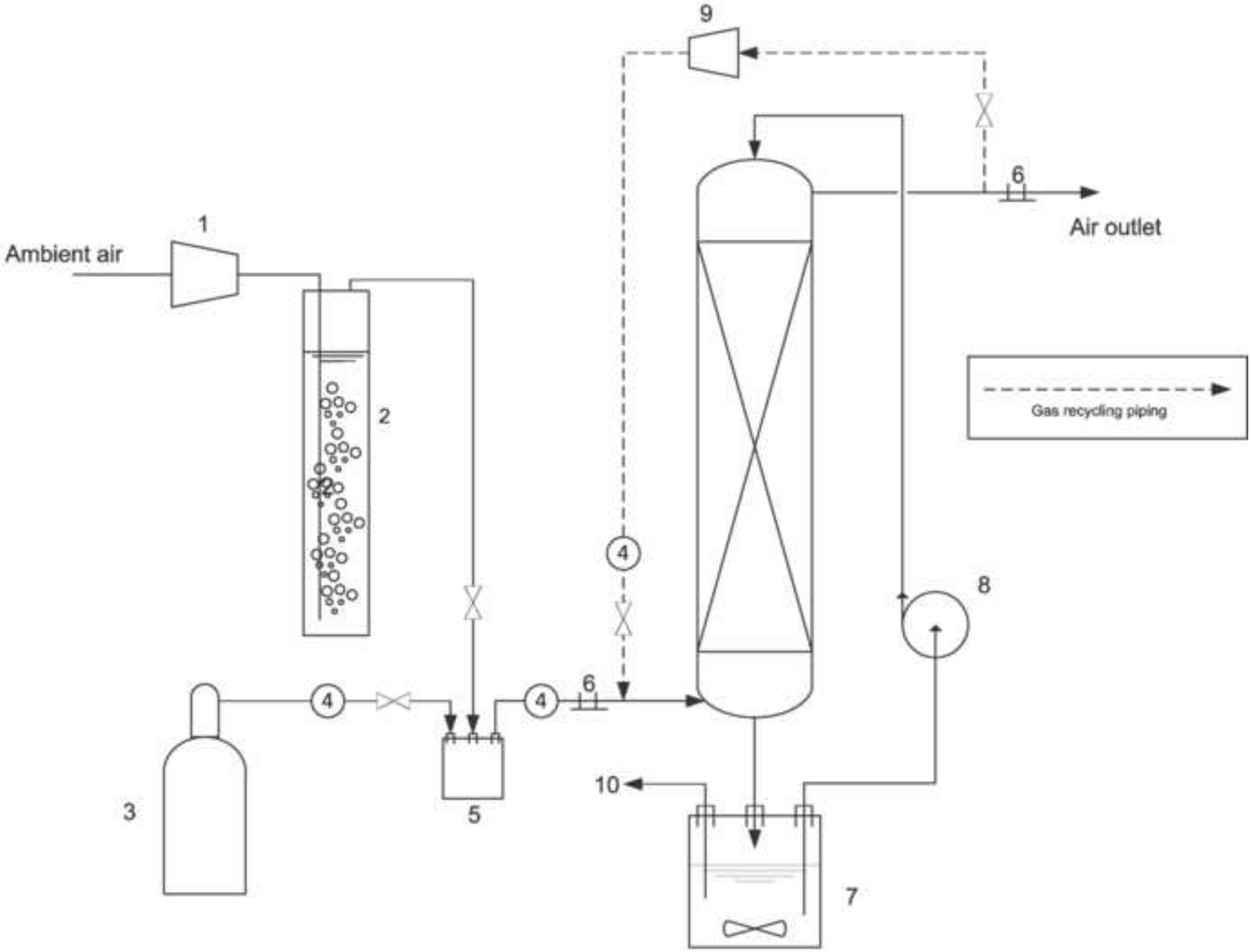

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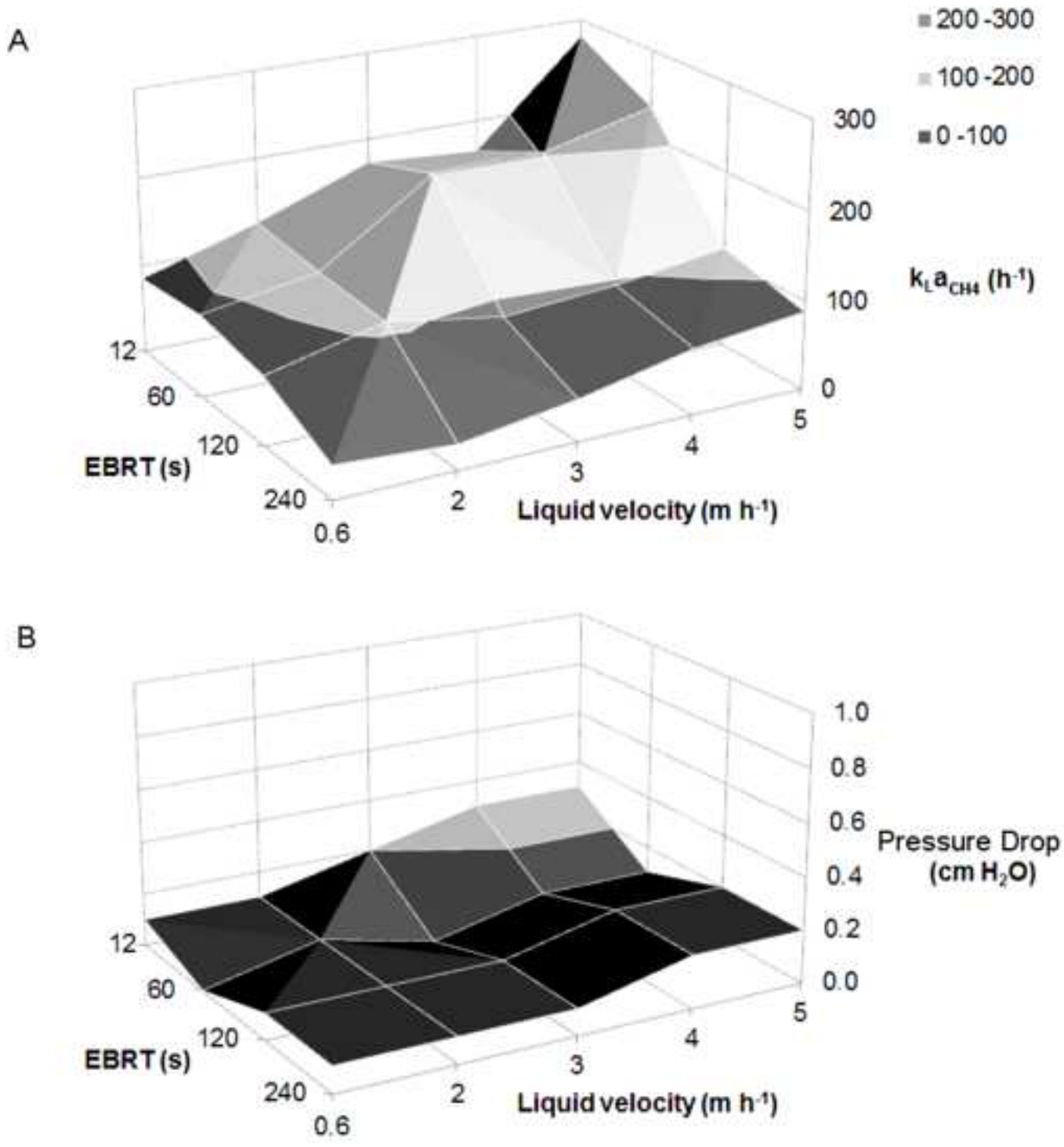

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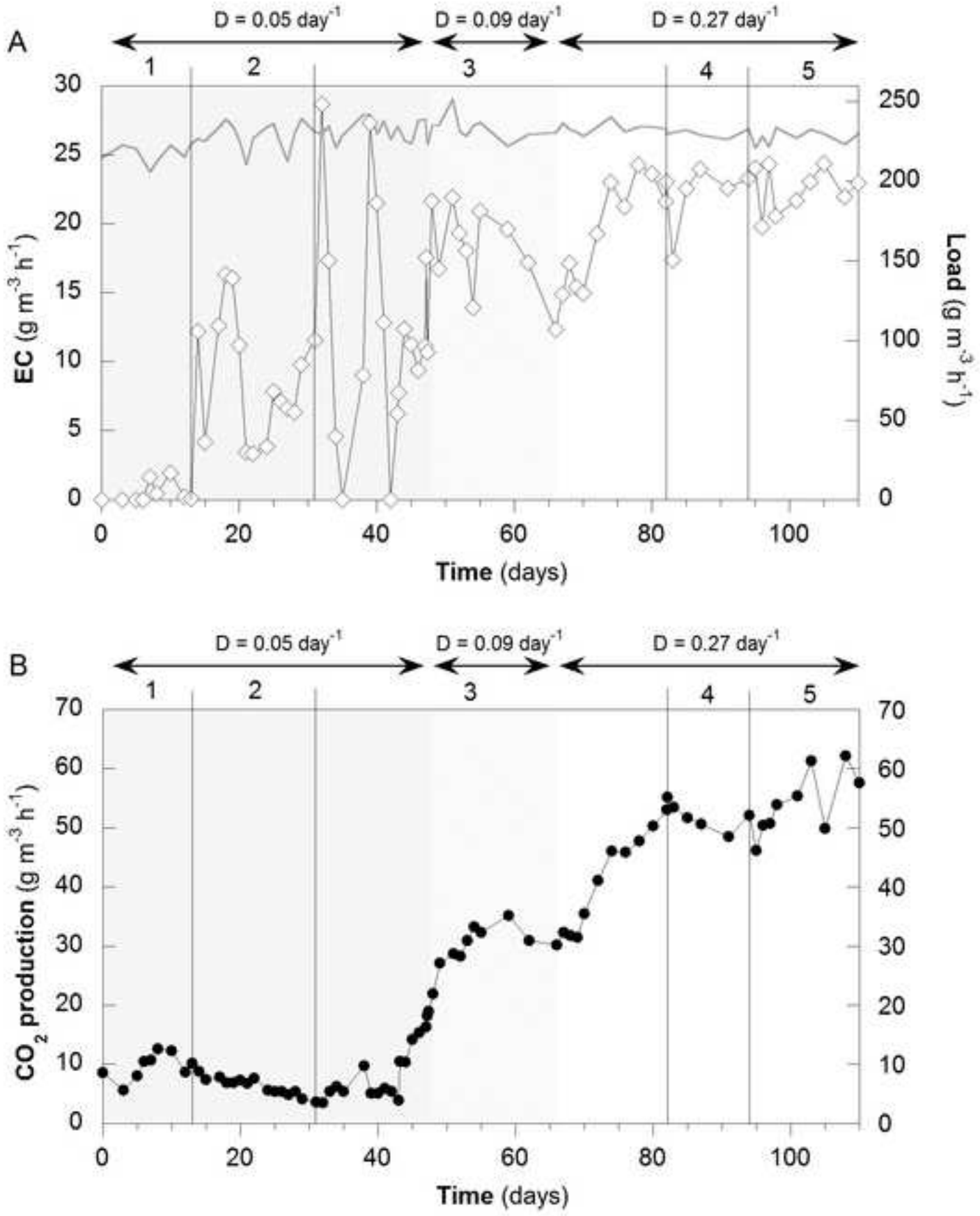

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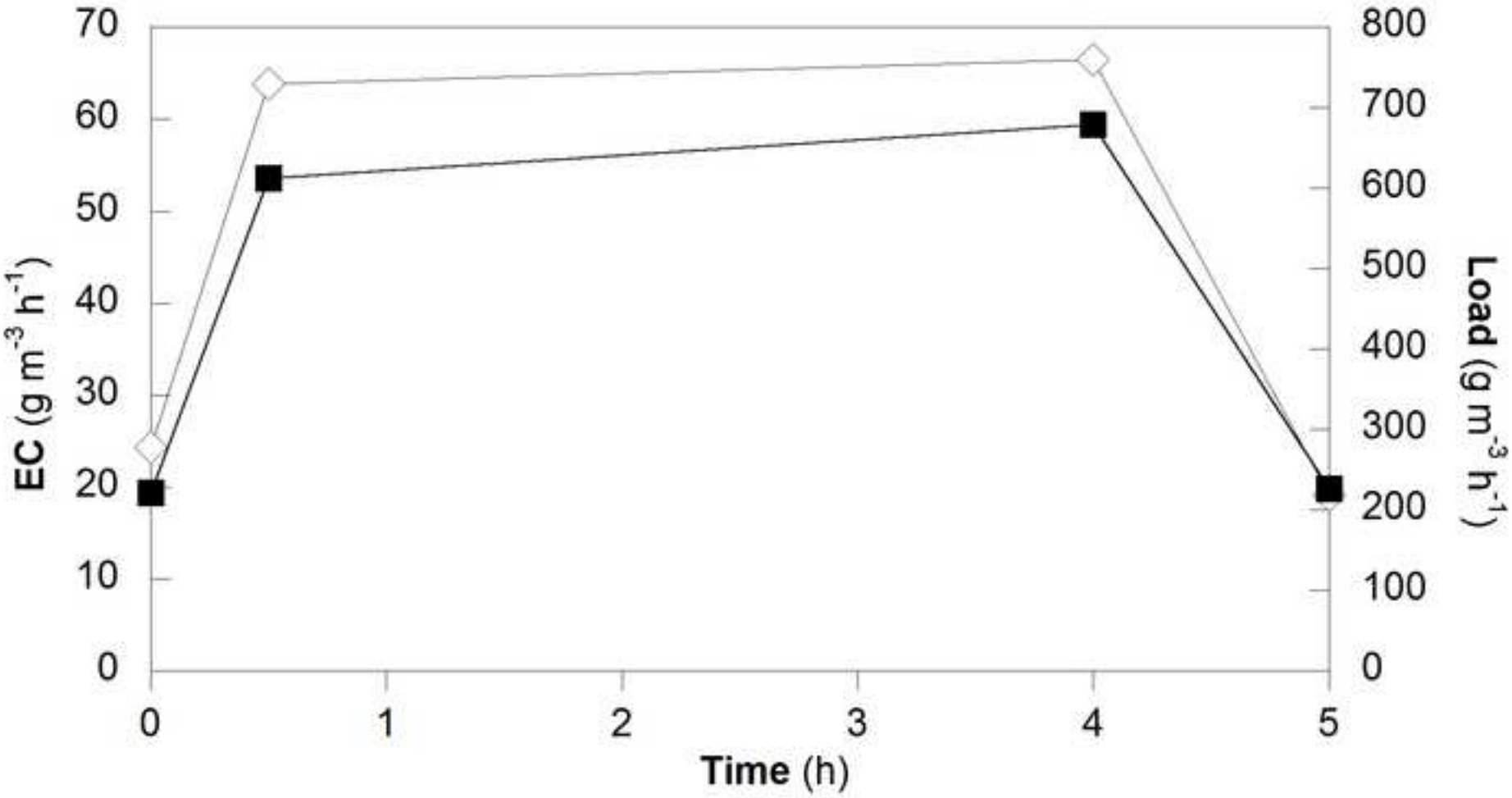

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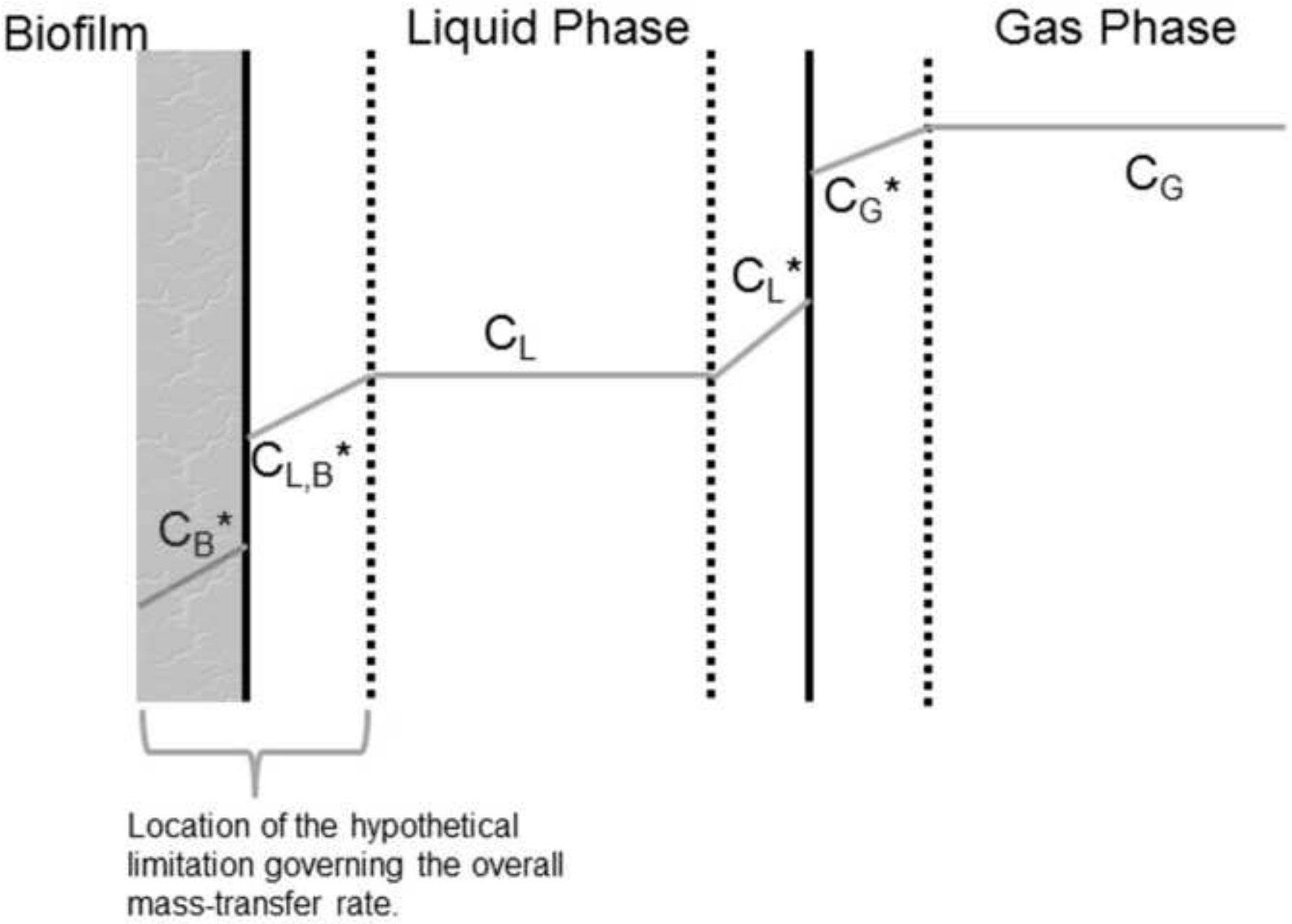
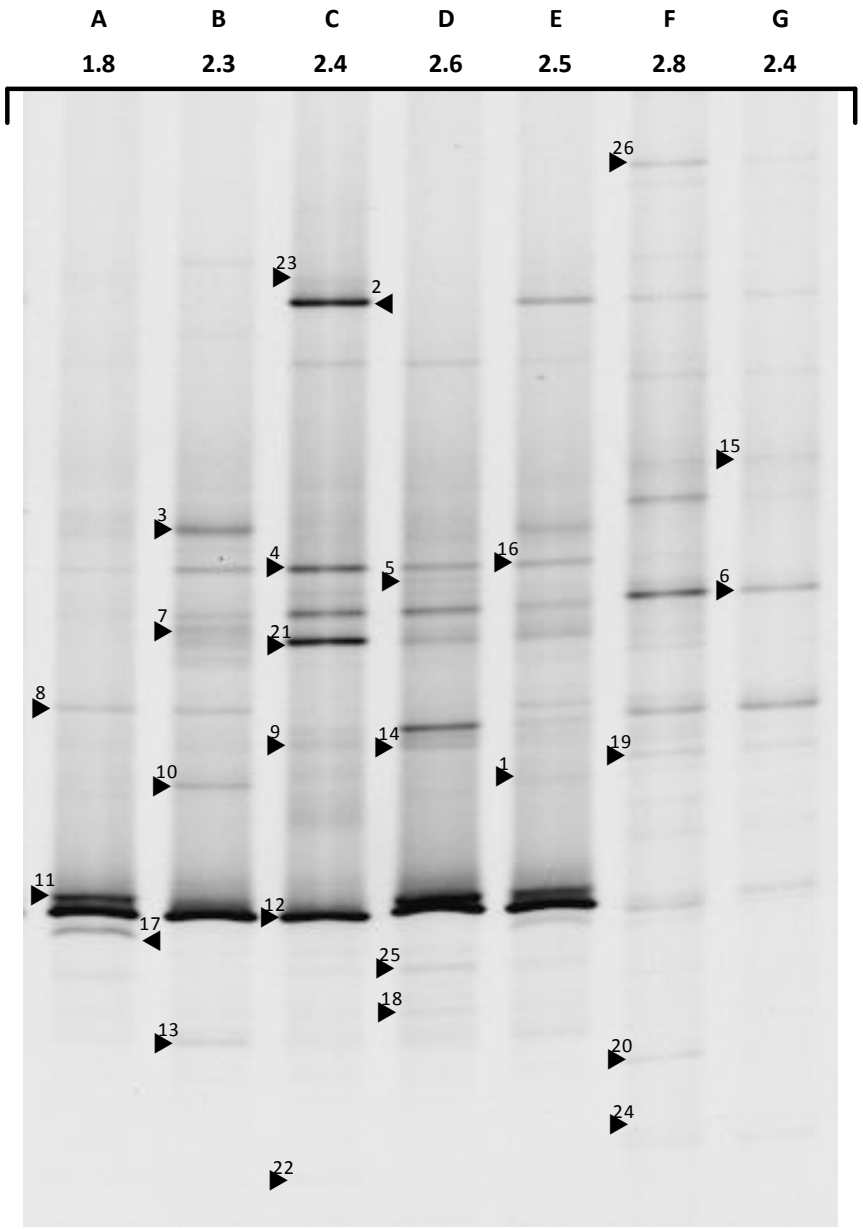


Figure 6

Figure 6.



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