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

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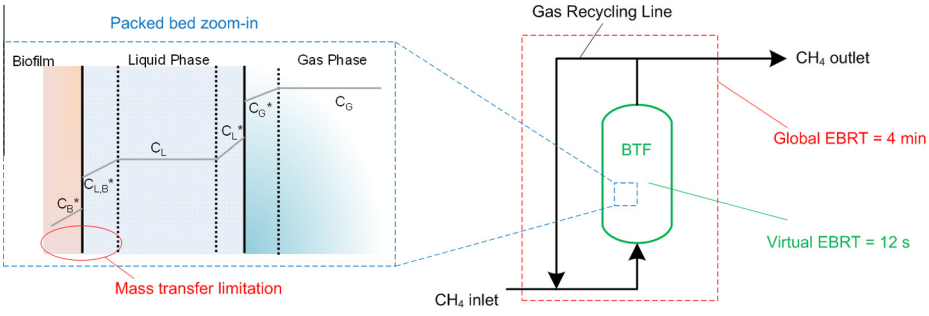
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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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} higher than most ECs achieved in single phase BTFs to date. The BTF exhibited a high microbial diversity (Shannon–Wiener indices of 2.5–2.8) dominated by Type I methanotrophs, 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.

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_4 emission 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%)

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[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 $k_La_{CH_4}$ 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 (g L^{-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 °C 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) (Fig. 1). All experiments were carried out at 20 °C.

2.4. Influence of the EBRT and liquid recycling on $k_La_{CH_4}$ 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. [18]. The overall k_La values for CH_4were estimated from k_La_{O2} using the correlation reported by Yu et al. (Eq. (1)) [19]:

$$\frac{k_La_{CH4}}{k_La_{O2}} = \frac{(1/V_{m,CH_4})^{0.4}}{(1/V_{m,O_2})^{0.4}} \quad (1)$$

where the mass transfer coefficient of a target gas pollutant ($k_La_{CH_4}$) 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}. This loading rate is high when compared to standard biofilters devoted for CH_4 abatement due to the lower EBRTs typically applied in BTFs, since they support a better mass transfer between the gas and liquid phases. 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 (Fig. 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