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Research article

A systematic comparison of two empirical gas-liquid mass transfer determination methodologies to characterize methane biodegradation in stirred tank bioreactors

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ABSTRACT

This study aimed at systematically comparing the potential of two empirical methods for the estimation of the volumetric CH_4 mass transfer coefficient (k_la_{CH4}), namely gassing-out and oxygen transfer rate (OTR), to describe CH_4 biodegradation in a fermenter operated with a methanotrophic consortium at 400, 600 and 800 rpm. The k_la_{CH4} estimated from the OTR methodology accurately predicted the CH_4 elimination capacity (EC) under CH_4 mass transfer limiting conditions regardless of the stirring rate (~9% of average error between empirical and estimated ECs). Thus, empirical CH_4-ECs of 37.8 ± 5.8, 42.5 ± 5.4 and 62.3 ± 5.2 g CH_4 m^{-3} h^{-1} *vs* predicted CH_4-ECs of 35.6 ± 2.2, 50.1 ± 2.3 and 59.6 ± 3.4 g CH_4 m^{-3} h^{-1} were recorded at 400, 600 and 800 rpm, respectively. The rapid Co^{2+}-catalyzed reaction of O_2 with SO_3^{-2} in the vicinity of the gas-liquid interphase during OTR determinations, mimicking microbial CH_4 uptake in the biotic experiments, was central to accurately describe the k_la_{CH4}.

1. Introduction

The assessment of current global greenhouse gas (GHG) emissions based on the 1-year pulse emission analysis has confirmed that CH_4 entails a contribution in terms of global warming potential (GWP) or global temperature change potential comparable to that of CO_2 for short time horizons (IPCC, 2013). This fact can be attributed to the high GWP of CH_4 (90 and 72 on a 10 and 20 years horizon, respectively) (Dessus et al., 2009). However, despite the environmental relevance of CH_4 emissions, the development of cost-efficient and environmentally friendly treatment technologies (especially of those intended for the treatment of diluted emissions where no energy recovery is technically feasible) has been scarce. Today, physical/chemical CH_4 abatement technologies, such as activated carbon adsorption and incineration, are either inefficient or costly at the low concentrations typically found in emissions from waste treatment facilities (except young landfills), mines and animal farms, and possess a large CO_2 footprint as a result of their intensive energy use (Estrada et al., 2012; Melse and Van Der Werf, 2005).

Biological methods represent an environmentally friendly alternative to physical/chemical methods for the abatement of CH_4. Biotechnologies, which rely on the biocatalytic action of specialized microorganisms, have been consistently proven as robust and efficient methods for the treatment of malodorous and industrial volatile organic compounds, exhibiting lower operating costs and environmental impacts than their physical/chemical counterparts (Estrada et al., 2012; Ferdowsi et al., 2017; Lopez et al., 2014). However, the cost-efficient application of conventional biotechnologies such as biofiltration or biotrickling filtration for the abatement of CH_4 is often limited by the poor mass transfer of this GHG from the gas emission to the methanotrophic community. This entails the need for large gas residence times (0.1–10 h), and therefore large bioreactor volumes and investment costs, which typically jeopardizes the economics of CH_4 abatement (Lopez et al., 2013). In this context, the bioconversion of CH_4 into added-value products in stirred tank bioreactors represents a promising alternative to enhance the economic sustainability of CH_4 abatement (Garcia-Perez et al., 2018; Karthikeyan et al., 2015; Pieja et al., 2012). Indeed, CH_4 can be bioconverted into biopolymers, ectoine,

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protein, exopolysaccharides, etc., using a biorefinery approach (Cantera et al., 2017). The development of cost-competitive CH_4 biorefineries, inherently limited by CH_4 supply to the microbial community, requires the development of accurate methodologies for the characterization of CH_4 gas-liquid mass transfer in conventional fermenters (Cantera et al., 2017). Unfortunately, the validation of empirical methodologies for the determination of the volumetric CH_4 mass transfer coefficient ($k_l a_{CH4}$) has been poorly addressed in literature (García-Ochoa and Gomez, 2009; Rocha-Ríos et al., 2010). Indeed, the lack of cheap and reliable dissolved CH_4 sensors along with the low solubility and limited industrial interest of CH_4 to date have restricted the development of accurate methodologies for the characterization of $k_l a_{CH4}$. Table S1 presents the main studies devoted to the characterization of the volumetric CH_4 mass transfer coefficients in bioreactors.

This study aims at comparing and validating, for the first time, two experimental methodologies for the estimation of $k_l a_{CH4}$ (gassing-out *vs* oxygen transfer rate methods) in order to accurately describe CH_4 abatement in a stirred tank reactor operated with a methanotrophic consortium at multiple stirring rates. This information is expected to provide the basis for a correct bioreactor design for CH_4 bioconversion into added-value products.

2. Material and methods

2.1. Microorganism and mineral salt medium

A mixed methanotrophic bacterial consortium containing *Sphingobacterium* sp. CZ-UAM (GenBank KJ411920) was used for CH_4 biodegradation purposes (Steffani-Vallejo et al., 2017). The consortium was enriched from the UAM-Iztapalapa wastewater treatment plant (México City). The composition of the mineral salt medium (MSM) used in the experiments was as follows (g l^{-1}): K_2HPO_4 0.7, KH_2PO_4 0.54, $MgSO_4{\cdot}7H_2O$ 1, $CaCl_2{\cdot}2H_2O$ 0.2, $FeSO_4{\cdot}7H_2O$ 0.004, NH_4CL 0.5, $ZnSO_4{\cdot}7H_2O$ 0.1, $MnCl_2{\cdot}4H_2O$ 0.03, H_3BO_3 0.3, $CoCl_2{\cdot}6H_2O$ 0.2, $CuCl_2{\cdot}2H_2O$ 0.01, $NiCl_2{\cdot}6H_2O$ 0.02 and $NaMoO_4{\cdot}2H_2O$ 0.06 (ATCC medium 1683). All chemicals were purchased from Sigma-Aldrich (USA). CH_4 (99.9%) was obtained from Praxair (Mexico).

2.2. Determination of the volumetric CH_4 mass transfer coefficient

A 3.5 L *ez*-control fermenter (Applikon, The Netherlands) equipped with two rushton turbines and containing 2.5 L of MSM was used for the determination of the volumetric mass transfer coefficient of O_2 ($k_l a_{O2}$) using the gassing-out and the oxygen transfer rate (OTR) methods (Quijano et al., 2009; Estrada et al., 2014). The $k_l a_{O2}$ was recorded at an aeration rate of 0.42 L min^{-1} under three stirring rates (400, 600 and 800 rpm) at 30 °C. These aeration rates were selected as potential operational conditions implemented in large-scale fermenters devoted to the bioconversion of CH_4.

In the gassing-out method, the MSM was initially degassed inside the fermenter for 15 min with argon at 0.42 L min^{-1} at the corresponding stirring rate (to complete dissolved O_2 depletion) and the dissolved O_2 concentration (DO) was then recorded every 5 s following the initiation of the aeration. The tests were carried out in duplicate using both polarographic and luminescent/optical dissolved O_2 sensors calibrated before each experimental series. The $k_l a_{O2}$ (h^{-1}) was determined using equation (1):

$$k_l a_{02} = -ln\left(\frac{C^*_{O_2L} - C_{O_2,L}}{C^*_{O_2L} - (C_{O_2,L})_0}\right) \Big/ t \quad (1)$$

where $C^*_{O_2L}$ stands for the dissolved O_2 concentration at saturation (6.75 mg L^{-1} at Mexico city at 30 °C), $C_{O_2,L}$ the dissolved O_2 concentration at time *t*, and $(C_{O_2,L})_0$ the dissolved O_2 concentration at the beginning of the test (DO = 0 mg L^{-1} at *t* = 0 s, since the cultivation broth was initially degassed with argon). In addition, a similar test series as above described was conducted with MSM supplemented with 0.03 M Na_2SO_3.

The OTR (g L^{-1} h^{-1}) from the gas phase to the MSM was estimated (in duplicate) by periodically monitoring the time course of SO_3^{-2} oxidation in the fermenter according to Quijano et al. (2009). The bioreactor was initially filled with 2.5 L of MSM containing sodium sulfite at 0.03 M and aerated for 30 min prior to the test. The kinetics of O_2 absorption were recorded after the addition of the catalyst (5 ml of a 2.5×10^{-4} M $CoSO_4$ solution, which supports an instantaneous SO_3^{2-} oxidation) until complete SO_3^{-2} depletion according to equation (2).

$$SO_3{}^{2-} + 0.5\ O_2 \xrightarrow{Co^{2+}} SO_4{}^{2-} \quad (2)$$

Aqueous samples of 5 mL were drawn from the bulk phase of the fermenter and SO_3^{-2} concentration was determined by iodometric back-titration according to Zhao et al. (1999). The $k_l a_{O2}$ was determined using equation (3):

$$k_l a_{02} = \frac{OTR}{\frac{C_{O_2,G}}{H_{02}} - C_{O_2,L}} \quad (3)$$

where OTR is calculated from the slope of the absorbed O_2 concentration (estimated from the SO_3^{-2} concentration multiplied by the O_2/SO_3^{2-} stoichiometric coefficient derived from equation (3)) versus time plot, H_{O2} stands for the dimensionless Henry law constant of O_2 (30.9 at 30 °C) and $C_{O2,G}$ represents the gas O_2 concentration in the exhaust gas (Zhao et al., 1999). Finally, the volumetric mass transfer coefficient of CH_4 was estimated from $k_l a_{O2}$ according to Yu et al. (2006) using the correlation empirically validated for stirred tank reactors based on dissolved CH_4 measurements and a dynamic methodology to characterize $k_l a_{O2}$ (equation (4)):

$$k_l a_{CH4} = \frac{k_l a_{O2}}{1,16} \quad (4)$$

2.3. Determination of the influence of the stirring rate on CH_4 elimination capacity

The 3.5 L *ez*-control fermenter equipped with two rushton turbines was initially filled with 2.5 L of MSM and inoculated with the bacterial consortium. The bioreactor was continuously supplied with a CH_4-laden air emission (0.42 L min^{-1}) at a CH_4 concentration of 26.9 ± 1.7 g m^{-3} and Cu-supplemented MSM (50 μg L^{-1} of $CuSO_4$) at a dilution rate of 0.12 d^{-1}. The temperature and pH of the cultivation broth were automatically controlled at 30 °C and 7, respectively. The system was initially operated for 60 days at 800 rpm to reach a steady state biomass concentration of 2.5 ± 0.4 g L^{-1} in order to prevent process limitation by microbial activity. The influence of the stirring rate (800, 600 and 400 rpm) on the CH_4 elimination capacity (EC) was evaluated by monitoring the inlet and outlet CH_4 gas concentration ($C_{CH4,in}$ and $C_{CH4,out}$, respectively) for at least 7 consecutive days at each stirring rate. The EC was calculated according to equation (5):

$$EC = \frac{C_{CH4,in} - C_{CH4,out}}{C_{CH4,in}} \quad (5)$$