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Nitrous oxide Production in Membrane-aerated Nitrifying Biofilms: Experimentation and Modelling

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Counter-diffusion biofilms; N_2O production; Nitrifying process

Summary

- N_2O emission including both bulk and gas phase is measured in counter-diffusion nitrifying biofilms under various operation conditions.
- Heterotrophs could be key contributors to N_2O production within counter-diffusion biofilms, even considering only the carbon source released from hydrolysis of decay products.
- A 1-D multispecies nitrifying biofilm model incorporating pH calculation and N_2O production/consumption pathway description was developed and calibrated.
- An in-depth understanding of N_2O production mechanism within counter-diffusion biofilms is studied, furthering the optimization of strategies to minimize its emission.

Introduction

Membrane-aerated biofilm reactors (MABRs) are excellent candidates to perform autotrophic nitrogen (N) removal process (Terada, Yamamoto, et al., 2006). In MABRs N oxidizing bacteria (ammonium oxidizers, AOB and nitrite oxidizers, NOB) thrive at the base of the biofilm, where oxygen is supplied from the membrane lumen. The other nutrients, including N source etc., are provided from the counter-side bulk phase, thereby flexibly decoupling the oxygen and substrate sources. Aiming at a short-cut ammonium (NH_4^+) removal or a one-stage nitritation-Anammox process in MABRs, controlling of the aeration regimes is an efficient approach to suppress NOB at the biofilm base and favour the growth of anaerobic ammonium oxidizers (AMX) in the outer anoxic biofilm layers (Pellicer-Nàcher, Sun, et al., 2010). However, the strong spatial gradients of nitrogenous species and oxygen within this counter-diffusion biofilm, especially in a dynamic aeration regime, may promote emissions of nitrogen oxides (N_xO) (Kampschreur, Tan, et al., 2008) (Ni and Yuan, 2013). Nitrous oxide (N_2O) and nitric oxide (NO) are atmospheric trace gases, of which N_2O is known as a greenhouse gas with a warming potential 300 times stronger than carbon dioxide. Therefore, an understanding of the N_2O production/dynamics in MABR system would be highly valuable for its further application.

Our main objective is to identify N_2O production mechanism in a lab-scale nitrifying MABR via a model-based exploration. The 1-D multi-species nitrifying biofilm model, incorporating N_2O production pathway descriptions, will be calibrated and validated with different experimental scenarios.

Materials and Methods

Reactor operation and N_2O measurement

The lab-scale MABR used PDMS membranes (3100506, Labmarket, Germany) and was inoculated with nitrifier-enriched biomass. Synthetic wastewater with NH_4^+ or NO_2^- was fed to provide various experimental scenarios. Aeration strategies (continuous or intermittent aeration) were switched to observe different reactor performance: continuous aeration was 100% air flowing through in the membrane lumen; intermittent aeration consisted of a 6-hour aeration (100% air) followed by a 6-hour non-aeration (100% N_2). Bulk N species were recorded; bulk DO and pH were monitored. N_2O was measured in the bulk liquid phase and within the biofilm with micro-electrodes, and in the lumen gas phase in each experimental scenario. Furthermore, net volumetric N_2O consumption or production rates were estimated from the respective concentrations profiles by using the Fick's second law of diffusion and Microsoft EXCEL add-ins solver were applied for the calculations as described previously (Lorenzen, Larsen, et al., 1998)

Modelling description

The multi-species biofilm model developed by Ma and Domingo-Félez, et al. includes microbial growth of AOB, NOB, AMX and heterotrophs and takes into account pH calculations and its effects on biological activities. In this study the model is extended to model processes relevant to N_2O production and consumption. Specifically, AOB related processes (nitrifier nitrification, NN and nitrifier denitrification, ND) are modelled following Domingo-Félez and Smets (2016) whilst denitrification by HB (HD) is modelled as suggested by Hiatt and Grady (2008). Consistent with experimental studies, the biological model considers NO as the direct precursor of N_2O in all three biologically-driven pathways. The model describes all relevant N_2O production pathways with fewer parameters than other biological models, thereby simplifying the calibration process. Transient N_2O accumulation on the aeration/non-aeration switch is modelled by multiplying the maximum process rate with a dynamic function as suggested by Schreiber and Loeffler, et al. (2009).

Model calibration and validation

In the calibration procedure, the model is fitted to experimental data by estimating a set of significant parameters based on sensitivity analysis. Then the model is subject to validation with reactor performance in other scenarios.

Table 1 Experimental scenarios in the N_2O model calibration and validation

Model calibration (short-term)	Influent concentrations	Aeration regime
	75 mg/L NH_4^+ + 20 mg/L NO_2^-	Air
	75 mg/L NH_4^+ + 20 mg/L NO_2^-	N_2
Model validation	Influent concentrations	Aeration regime
	75 mg/L NH_4^+	Air or Air/N_2
	75 mg/L NH_4^+ + 20 mg/L NO_2^-	Air/N_2
	75 mg/L NH_4^+ + increased buffer	Air or Air/N_2

Results and Discussion

In the long-term reactor operation, a nitrifying biofilm readily developed when the MABR was initially operated under continuous aeration: NO_3^- was the dominant NO_x^-_N species in the

effluent and NO_2^-_N/NO_x^-_N was around 5% after 2 months operation, suggesting active NOB activity with continuous aeration (Figure 1). Meanwhile, almost no N loss showed minor AMX activity. Total N_2O emission under continuous aeration was ca. 2.35% of the total N loading, and N_2O in the gas phase which was typically not reported in other counter-diffusion biofilms was comparable to the liquid phase (Table 2). At day 67, MABR was switched to intermittent aeration (6-hour aeration and 6-hour non-aeration), promoting NOB suppression and increased AMX activity, caused the instant absence of NO_2^- in the bulk. N loss increased due to activated AMX. Noticeably, N_2O emission decreased to 0.32% of the total N loading.

Table 2 N_2O emission in the lab-scale MABR under different aeration regimes (R1-R4)

		N_2O emission (% of N loading)	
Time (days)	Aeration regime	Bulk phase	Gas phase
R1: 50-67	Air	1.31 ± 0.35	1.23 ± 0.38
R2: 68-95	Air/N_2	0.01	0.34
R3: 96-143	Air	0.22	0.32
R4: 144-196	Air/N_2	0.07	0.11

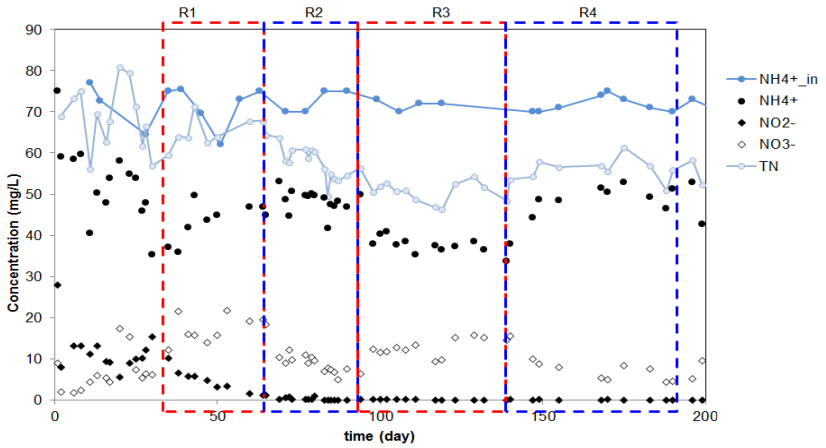

Figure 1 Long-term MABR performance under different aeration regimes (R1-R4) - Nitrogen concentrations in the bulk. Short-term reactor performances (including relevant microprofiles) are not shown here.

N_2O microprofiles within the biofilm were measured under continuous/intermittent aeration regime (Figure 2A). In continuous aeration (R1) N_2O was significantly produced at the biofilm top and bottom; while N_2O was only produced at the biofilm bottom in intermittent aeration (R2) (Figure 2B). It suggested that HD pathway was easily underestimated within counter-diffusion biofilm as reported (Pellicer-Nàcher, Sun, et al., 2010). In the next step, significant parameters in the N_2O biofilm model will be estimated with short-term experimental data, including N_2O microprofiles within the biofilm which were typically not used in other N_2O model calibrations. The calibrated model will be validated with long-term reactor performance and N_2O production. Therefore, the individual contribution of each N_2O production pathway to its total emission can be evaluated; moreover, the significance of intermittent aeration in mitigation N_2O emission in MABRs can be highlighted by comparison to continuous aeration (Figure 2). An in-depth understanding of N_2O production mechanism within counter-diffusion

biofilms is elaborated, thus strategies to minimize its emission in this system can be proposed.

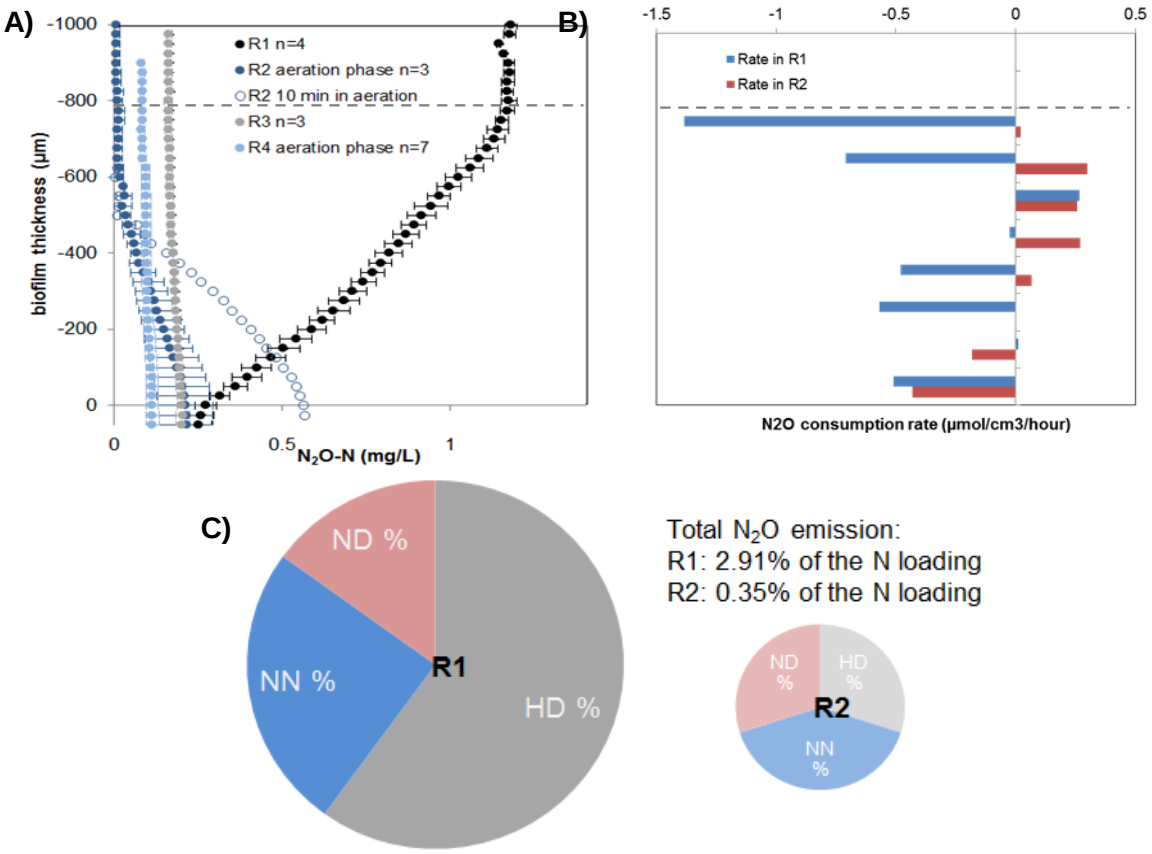

Figure 2 A) Averaged N_2O microprofiles within the biofilm; B) Spatial distributions of net volumetric production/consumption rates of N_2O calculated from the average concentrations profiles in R1 and R2; C) Model-based evaluation of the individual contribution of each N_2O production pathway to the total N_2O emission under different aeration regimes (R1-continuous aeration; R2- intermittent aeration)

Conclusion

In counter-diffusion nitrifying biofilms, N_2O emission in the gas phase, which was usually underestimated, was comparable to the liquid phase. Heterotrophs could be key contributors to N_2O production within counter-diffusion biofilms, which should be highlighted even considering only the carbon source released from hydrolysis of decay products. In the calibration of N_2O biofilm models, performance within the biofilm showed higher sensitivity compared to the bulk performance. Both the experimentation and modelling showed that intermittent aeration was an efficient means to mitigate N_2O emission in the MABRs.

Acknowledgement

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