

Oxygen Penetration Depth as a Tool to Predict Nitrous Oxide Emissions from Granular Partial Nitritation Wastewater Treatment Systems

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Shorth Abstract/Workshop Description

Six Nitrous Oxide (N₂ O) emission tests, corresponding to combinations of three dissolved oxygen and two temperature levels, were performed on a lab-scale granular Partial Nitritation (PN) reactor. Emission factors (EF_{N₂O}) ranged from 0.60 to 2.97 % of the Ammonium Oxidation Rate, and were negatively correlated with the granules' estimated oxygen penetration depths (δ_{O_2}). The ratio between anoxic and aerobic granule volume, easily derivable from δ_{O_2} , was linearly correlated with EF_{N₂O} ($R^2=0.91$), and was therefore proposed as a tool to predict N₂ O emissions from PN granules. This study lays the foundations for future works aimed at refining the proposed EF_{N₂O} prediction method.

Permission to publish

yes

Extended Abstract Submission / Workshop Details

Introduction

The effort in developing efficient processes for nitrogen removal from wastewater has intensified research on strategies to achieve Partial Nitritation (PN) in the mainstream line of Wastewater Treatment Plants (WWTPs). This would allow nitrogen removal via the nitrite instead of the nitrate pathway, reducing aeration energy consumptions and resulting CO₂ emissions compared to Conventional Activated Sludge (CAS). However, some studies suggest that PN could lead to increased emissions of Nitrous Oxide (N₂ O), a greenhouse gas with a GWP of 274 [1]. Developing a reliable method to predict N₂ O emissions from PN systems based on operational conditions would be crucial to quantify the actual overall environmental advantage of PN over CAS, and to optimize the systems' design parameters. This study assesses the effect of oxygen penetration depth (δ_{O_2}) inside granular sludge performing PN on its N₂ O emission factors (EF_{N₂O}), aiming to assess whether δ_{O_2} could be used for EF_{N₂O} prediction methods.

Materials and Methods

Six N₂ O emission tests, corresponding to combinations of two temperatures and three Dissolved Oxygen (DO) levels, were performed inside a lab-scale granular biomass SBR reactor performing PN. The reactor was hermetically sealed, with a peristaltic pump conveying the produced off-gas from the headspace to a sampling bag throughout each test. After each cycle, a micro-gas chromatograph was used to quantify the N₂O accumulated in the bag. Each cycle's total N₂O emissions were estimated by measuring the air volumes introduced into the reactor using a mass flowmeter, and normalized to the total ammonium oxidized to obtain EF_{N₂O} · δ_{O_2} in each condition was calculated with (i) a 1-D reaction-diffusion biofilm model, assuming Monod-type microbial kinetics, non-limiting ammonium, uniformly distributed biomass entirely consisting of Ammonium Oxidizing Bacteria (AOB) and (ii) Equation 1 [2] for comparison. Table 1 reports experimental and modeling parameters.

$\delta_{O_2} = \sqrt{\frac{2D_{O_2}DO}{r_{O_2}C_X}}$	(1)
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Table 1

Test name	-	LT-LDO	LT-SDO	LT-HDO	HT-LDO	HT-SDO	HT-HDO
Temperature (T)	°C	11.8 ± 0.5	13.0 ± 0.5	13.0 ± 0.5	20.8 ± 0.2	20.0 ± 0.3	20.3 ± 0.1
Dissolved oxygen (DO)	mgO ₂ · L ⁻¹	2.0 ± 0.2	4.1 ± 0.5	6.0 ± 0.5	1.9 ± 1.0	3.7 ± 0.8	5.6 ± 0.2
Oxygen diffusion coefficient (D _{O2})	10 ⁻⁵ cm ² · s	1.12	1.16	1.16	1.44	1.41	1.42
Mean granule radius (R _g)	µm	559			485		
Maximum oxygen uptake rate at 20 °C (r _{O2,20°C})	mgO ₂ · gVSS ⁻¹ · h ⁻¹	6.7					
Oxygen half-saturation constant (K _o)	mgO ₂ · L ⁻¹	0.05					
Temperature coefficient (θ)	-	1.123					
Number of layers	-	500					
Biofilm density (C _x)	mgVSS · L ⁻¹	42.2					

Results and discussion

Test and simulation results are reported in Table 2.

Table 2

Test name	-	LT-LDO	LT-SDO	LT-HDO	HT-LDO	HT-SDO	HT-HDO
Ammonium Oxidation Rate (AOR)	mgN · L ⁻¹ · d ⁻¹	172.8	269.6	278.9	299.9	519.9	803.5
N ₂ O emission factor (EF _{N2O})	% of AOR	1.22	0.76	0.60	2.97	1.48	0.89
Oxygen penetration depth (model) δ _{O2,model}	µm	39	53	64	26	37	45
Oxygen penetration depth (analytic) δ _{O2,analytic}	µm	38.6	52.4	63.4	25.2	36.5	44.3

Experimental EF_{N2O} values ranged from 0.60 to 2.97 % of AOR. Figure 1 shows the correlation between δ_{O2,model} and EF_{N2O} for each test. The smooth and monotonic trend indicates an inverse correlation between the two variables, suggesting that emissions increased for thicker anoxic biofilm layers. This is coherent with studies imputing most N₂ O emissions in nitrification systems to nitrifier denitrification, a metabolic pathway in which AOB reduce nitrite to N₂ O in anoxic environment.

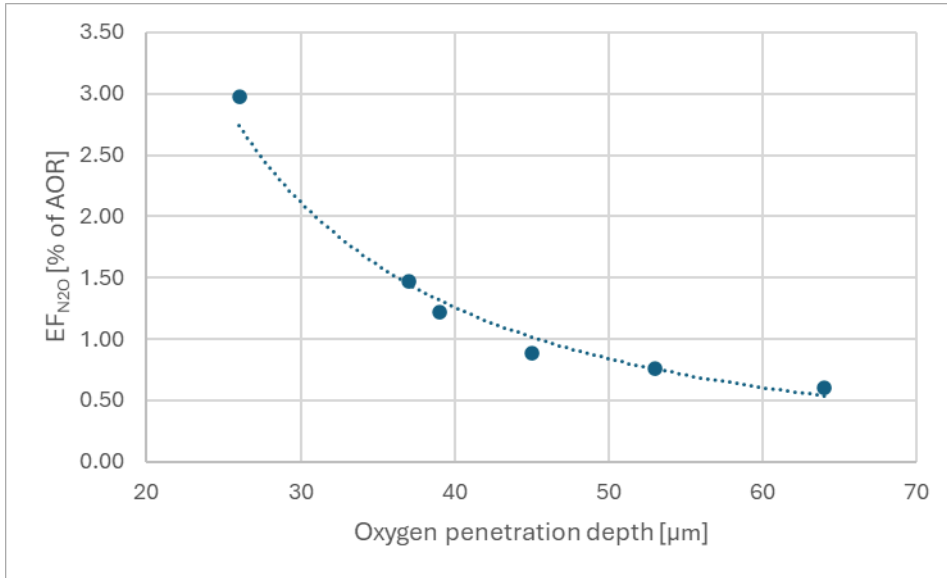


Figure 1

To develop a prediction method for N₂ O emissions, the peculiar shape of the curve must be explained. Equation 2, matching the definition of EF_{N2O}, was used for this purpose, assuming that N₂ O emissions were only occurring in the granules' anoxic layer.

$$EF_{N2O} = 100 \frac{N_2OR}{AOR} = 100 \frac{C_x r_{N2O,20^\circ C} \vartheta^{T-20} V_{anox}}{C_x r_{NH4,20^\circ C} \vartheta^{T-20} V_{aer}} \propto \frac{V_{anox}}{V_{aer}} \quad (2)$$

Where:

• N_2OR	N ₂ O emission rate;	
• $r_{N2O,20^\circ C}$	N ₂ O production rate (20 °C);	
• $r_{NH4,20^\circ C}$	NH ₄ ⁺ uptake rate (20 °C);	
• $V_{anox} = \frac{4}{3}\pi(R_g - \delta_{O2})^3$	Anoxic granule volume;	
• $V_{aer} = \frac{4}{3}\pi R_g^3 - V_{anox}$	Aerobic granule volume.	

The proportionality of V_{anox}/V_{aer} and EF_{N2O} was verified with the plot shown in Figure 2.

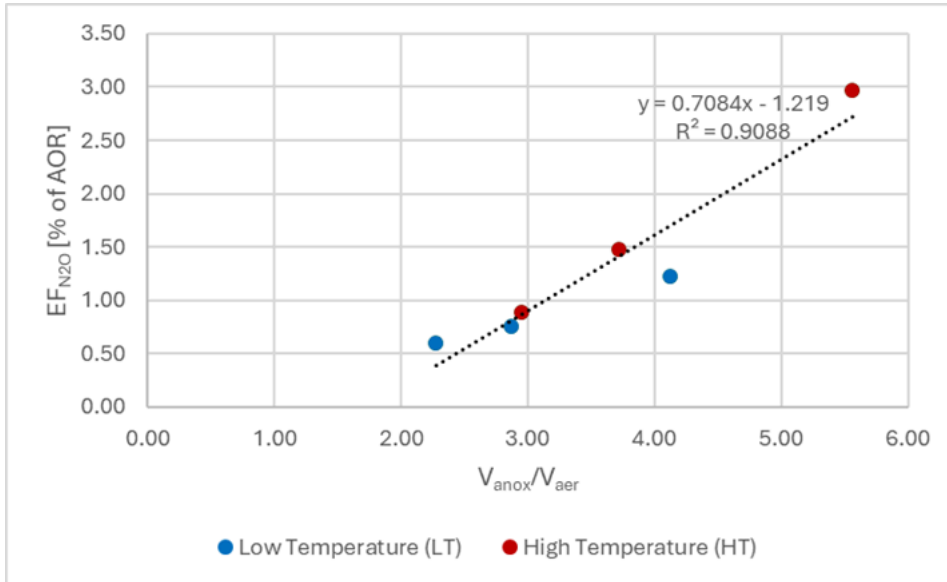


Figure 2

The good linear correlation ($R^2 = 0.91$) suggests that V_{anox}/V_{aer} can be used to predict EF_{N_2O} from PN granules. Nevertheless, two issues arise:

1. the regression's y-intercept is negative (-1.2%), suggesting that a minimum V_{anox} exists associated with null EF_{N_2O} . According to literature, however, some N_2O emissions can occur also aerobically, due to chemical hydroxylamine oxidation [1];
2. R^2 improves by considering the LT and HT tests separately, with both values exceeding 0.99.

Possible explanations for (i) are that (a) the correlation is not really linear, but has an exponential trend, for which a justification is still to be found; (b) the biomass in the granules' core could be mineralized, and therefore not contribute to N_2O production, shifting the actual graph to the left.

As for (ii), the different slopes of the LT and HT correlations could be imputed to different temperature correction values (θ) for the N_2O emission and NH_4^+ removal rates (see Equation 2). Temperature-dependent changes in the behaviour of hydroxylamine diffusion, which Sabba et al. [3] consider a critical factor affecting N_2O emissions from biofilms, could also be an explanation.

Further experiments are needed to confirm the validity of V_{anox}/V_{aer} as a EF_{N_2O} predictor, addressing issues (i) and (ii).

Conclusions

To date, predicting N_2O emissions from WWTPs remains a difficult task, as experimental EF_{N_2O} reported in literature fall into a wide range [1]. Simple (i.e. not relying on numerical models) but solid methods for EF_{N_2O} estimation based on easily determinable parameters such as DO and temperature would be crucial to better quantify the environmental impact of N removal processes, and to optimize the operational conditions for full-scale applications.

The results presented in this study make it clear that oxygen penetration depth strongly affects N_2O emissions from PN granules. The V_{anox}/V_{aer} ratio, which is derivable from δ_{O_2} and granule size, shows a promising potential for the prediction of emission factors, as it appears to be strongly correlated with EF_{N_2O} . Moreover, V_{anox}/V_{aer} can be calculated without much computational effort, as analytical values of δ_{O_2} do not differ significantly from the ones determined numerically (Table 1). However, the scarcity of data points available in this study and the two issues presented in the previous paragraph lead to the need for further research to establish a straightforward EF_{N_2O} prediction method. Future studies should include:

- A greater number of experimental data for better parameter estimation;
- Experiments performed in conditions designed to approach a null V_{anox}/V_{aer} ratio to address issue (i);
- A greater variability of temperatures used for experiments, to address issue (ii);
- Experiments performed with the same DO and temperature conditions (and thus same δ_{O_2}) on granules with different diameter.

Developing a simple EF_{N_2O} prediction method from PN granules could be the groundwork for similar studies on more complex types of biofilms, such as PN-Anammox and Aerobic Granular Sludge, leading towards the development of operational strategies to minimize the environmental impact of granular sludge WWTPs.

References

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Nitrous oxide emissions; Partial Nitritation; Granular Sludge

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