ASSESSMENT OF N_2O EMISSIONS IN A PARTIAL DENITRIFICATION PROCESS USING ROPE-TYPE BIOFILM MEDIA

Shewa W. A., Kobilnyk T., Bossy K., Bishop Water Inc.*, Sun L., Dagnew M., Western University

*16 Edward St. S Suite 203, Arnprior, ON, K7S 3W4, wudneh@bishopwater.ca

1. INTRODUCTION

The escalating concerns over global warming and climate change necessitate a deeper understanding and vigilant monitoring of greenhouse gas (GHG) production pathways and release during wastewater treatment processes (Ren et al., 2019). Nitrous oxide (N_2O), recognized as a principal GHG with a global warming potential 273 times higher than carbon dioxide (CO_2), has garnered considerable attention (Sabba et al., 2018), and it is of interest to understand how the emerging total nitrogen (TN) removal processes employed in wastewater treatment contribute to the production and emission of N_2O. The partial denitrification (PDN) (or denitration) process by terminating nitrate (NO_3) reduction at nitrite (NO_2) may limit N_2O precursor (nitric oxide) production. The nitrite generated in the PDN process is typically used as a substrate for the autotrophic anaerobic ammonia oxidation (anammox) process to remove TN. However, it is also possible that part of the nitrite may still be denitrified through the heterotrophic denitrification pathway. More importantly, accurate theoretical assessment becomes complicated for biofilm processes where several organisms co-exist within the biofilms. Despite the extensive literature on N_2O emissions from conventional wastewater treatment processes, there is a lack of in-depth studies exploring the level and behaviour of N_2O emissions in co-diffusion biofilm-based emerging nitrogen removal processes.

Enhancing the understanding of N_2O emissions in the PDN process necessitates the establishment of stable nitrite accumulation as a preliminary step. Carbon sources, acting as electron donors, including ethanol, acetate, glucose, glycerol, methanol, and internal wastewater carbon, play a significant role in the PDN process. The objectives of this study included (1) monitoring and quantifying the N_2O emissions in the biofilm-based partial denitrification process, (2) assessing the impact of varying COD/N ratios on PDN performance and N_2O emission mitigation, (3) evaluating the effects of scouring versus non-scouring-modes on N_2O emissions, nitrite accumulation, and overall total nitrogen removal in PDN biofilm reactors (4) examining the effectiveness of acetate and methanol as carbon sources for achieving stable and substantial nitrite accumulation.

2. METHODOLOGY

The partial denitrification study was conducted with BioCord® Reactors, manufactured by Bishop Water. BioCord Reactors are a fixed-film, semi-passive biological treatment process that enables wastewater lagoons and mechanical treatment plants to improve the removal of ammonia through nitrification and partial denitrification processes. This process intensification technology can be installed directly into wastewater lagoons or treatment basins and is proven to provide year-round ammonia removal even when wastewater temperature is near freezing.

The rope-type media provides a significant surface area to establish a robust, resilient biofilm and utilizes a fine-bubble aeration system powered by low-energy compressors to achieve optimal oxygen transfer, create a fully mixed zone, scour excess biofilm and prevent ice from forming around the treatment cell (Figure 1).

FIGURE 1. BIOCORD REACTORS ARE SHOWN BEING INSTALLED INTO A LAGOON CELL (LEFT) TO IMPROVE TREATMENT CAPACITY AND PERFORMANCE. THE ROPE-TYPE MEDIA (UPPER RIGHT) SUPPORTS THE GROWTH OF A ROBUST, COLD-TOLERANT BIOFILM (LOWER RIGHT) THAT INCREASES REMOVAL OF AMMONIA AND ORGANICS.

In this study, two bench-scale BioCord reactors (working volume of 2 L) operated for 267 days (Figure 2). The setup was maintained at room temperature (22°C). The reactors were employed with rope-type supporting media (BioCord) biofilm modules (specific surface area of 2.4 m^2/m). BioCord is a solid woven polypropylene material developed by Bishop Water Inc. (Shewa et al., 2024).

The reactors simulated a post-anoxic process with external carbon sources to achieve PDN and to understand the nitrous oxide emission under varying COD: N ratios and scouring modes. The nitrous oxide emission and associated TN removal were characterized by varying biofilm thickness, COD, and nitrogen loadings.

Prior to the nitrous oxide emission study, a preliminary study was conducted assessing the extent of PDN efficiency (nitrite accumulation) using two carbon sources (methanol and acetate) and operating at varying hydraulic retention times (HRTs) (2 and 5 hours). The operation scheme is summarized in Table 1.

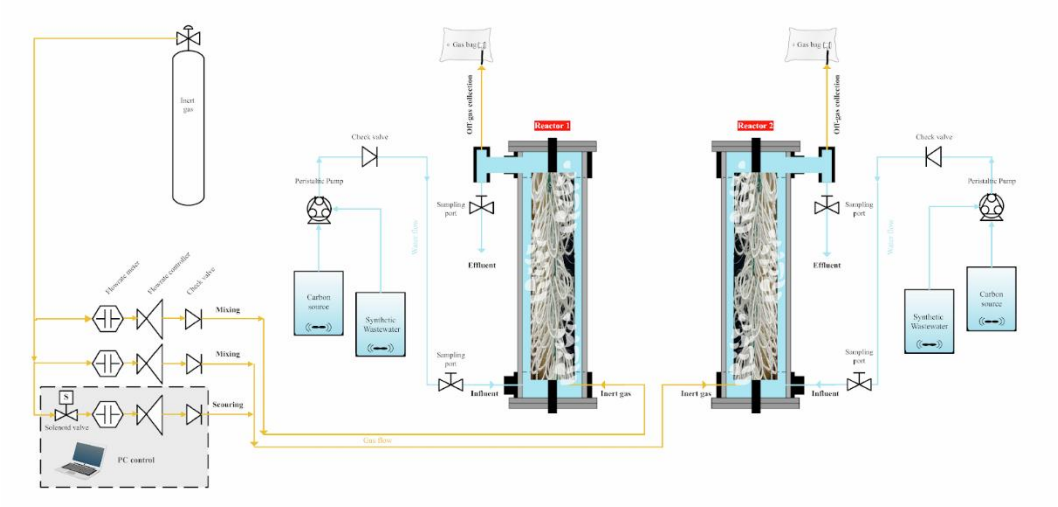

FIGURE 2: REACTOR SETUP SCHEMATICS

TABLE 1: THE OPERATION SCHEME OF REACTORS

Phases	Days	Inert gas	HRT (hr)	Designed COD/NO_3-N ratio	Off-gas collection	Reactors			
						R1 (control)		R2 (target)	
						Scouring	Carbon source	Scouring	Carbon source
Phase 1	38	N_2	2	3	No	No	Acetate	No	Acetate
Phase 2	17	N_2	2	2	No			No	Acetate
Phase 3	50	N_2	5	3	No			No	Methanol
Phase 4	33	N_2	5	1.5	No			No	Methanol
Phase 5	51	N_2	5	1.5	No			No	Acetate
Phase 6	27	Ar	5	1.5	Yes			500 mL/min, 2 mins per day	Acetate
Phase 7	62	Ar	5	3	Yes			500 mL/min, 2 mins per day	Acetate

In the bench reactors, the temperature, bulk liquid dissolved oxygen (DO), pH and bulk liquid oxidation-reduction potential (ORP) values were measured three times weekly. All wastewater samples were analyzed for NH_3-N, NO_3-N and NO_2-N concentrations (Standard Method 4500) employing a discrete analyzer (Seal Analytical AQ300). The soluble chemical oxygen demand (sCOD) was analyzed using Hach Method 8000. The off-gas were collected from the top of the reactors two to three times per week and analyzed using gas chromatography (GC) (Agilent Technologies, GC 7890B).

In this study, NO_3 removal efficiency, NO_2 accumulation efficiency, N_2O emission efficiency, NO_3 removal rate, NO_2 accumulation rate, and N_2O emission rate were calculated using Equations 1, 2, 3, 4, 5 and 6, respectively.

$$\mathrm{NRE} = \frac{(\mathrm{NO_3\text{-}N_{inf}}) - (\mathrm{NO_3\text{-}N_{eff}})}{(\mathrm{NO_3\text{-}N_{inf}})} * 100\% \quad (1)$$

$$\mathrm{NAE} = \frac{(\mathrm{NO_2\text{-}N_{eff}}) - (\mathrm{NO_2\text{-}N_{inf}})}{(\mathrm{NO_3\text{-}N_{inf}}) - (\mathrm{NO_3\text{-}N_{eff}})} * 100\% \quad (2)$$

$$\mathrm{NEE} = \frac{(\mathrm{N_2O\text{-}N_t}) - (\mathrm{N_2O\text{-}N_{t=0}})}{(\mathrm{NO_3\text{-}N_{inf}}) - (\mathrm{NO_3\text{-}N_{eff}})} * 100\% \quad (3)$$

$$\mathrm{NRR} = \frac{(\mathrm{NO_3\text{-}N_{inf}}) - (\mathrm{NO_3\text{-}N_{eff}})}{\mathrm{A}} * \mathrm{Q} * \mathrm{t_D} \quad (4)$$

$$\mathrm{NAR} = \frac{(\mathrm{NO_2\text{-}N_{eff}}) - (\mathrm{NO_2\text{-}N_{inf}})}{\mathrm{A}} * \mathrm{t_D} \quad (5)$$

$$\mathrm{NER} = \frac{(\mathrm{N_2O\text{-}N_t}) - (\mathrm{N_2O\text{-}N_{t=0}})}{\mathrm{A}} * \mathrm{t_D} \quad (6)$$

where: NRE = NO_3 removal efficiency
NAE = NO_2 accumulation efficiency
NEE = N_2O emission efficiency
NRR = NO_3 removal rate
NAR = NO_2 accumulation rate
NER = N_2O emission rate
Q = off-gas flow rate (L/min)
A = surface area per reactor (2.376 m^2)
t_D =1440 minutes per day
t = sampling time (min)
inf = influent
eff = effluent

3. RESULTS AND DISCUSSION

The nitrate removal, nitrite accumulation and N_2O emission of the post-anoxic PDN process under different carbon sources (acetate and methanol), COD/NO_3-N ratios (1.5, 2 and 3) and scouring modes (no scouring and daily scouring) were compared in reactors R1 and R2 over several months of operation. In this study, reactor 1 (R1) served as the control, operating with acetate as its sole carbon source and without inert gas scouring, comparable to the researchers' previous study (Sun et al., 2024). In contrast, the R2 reactor was subjected to varying experimental conditions, including the use of different carbon sources and the application of inert gas scouring modes.

3.1 Impact of HRT, COD and NO_3-N concentrations, and carbon source shift on nitrite accumulation performance in PDN biofilms

The NO_3-N removal rates, depicted in Figure 3, decreased when the COD/N ratio was reduced from 3 to 1.5 due to limited carbon availability in the R2 reactor, and further declined after switching from methanol to acetate in phase 5. The nitrate removal rates (NRR) were 0.65 ± 0.14, 0.50 ± 0.09, and 0.37 ± 0.12 g $N/m^2/d$ in phases 3, 4, and 5, respectively, corresponding to nitrogen removal efficiencies (NRE) of 86%, 67%, and 38%. Statistical analysis showed that these differences were insignificant compared to the control acetate-fed reactor (R1), which had NRR ranging from 0.40 ± 0.17 to 0.61 ± 0.17 g $N/m^2/d$. The biofilm's nitrate reduction capability in this study was comparable to that found in other research, achieving 69% NRE using methanol (Pan et al., 2023). It is well-documented that different carbon sources can enrich distinct microbial consortia, with varying efficiencies in nitrate reduction (Li et al., 2016). In our study, acetate and methanol achieved similar nitrate reduction rates in non-scoured PDN biofilms. Also, no significant differences were observed in COD removal rates when using methanol versus acetate.

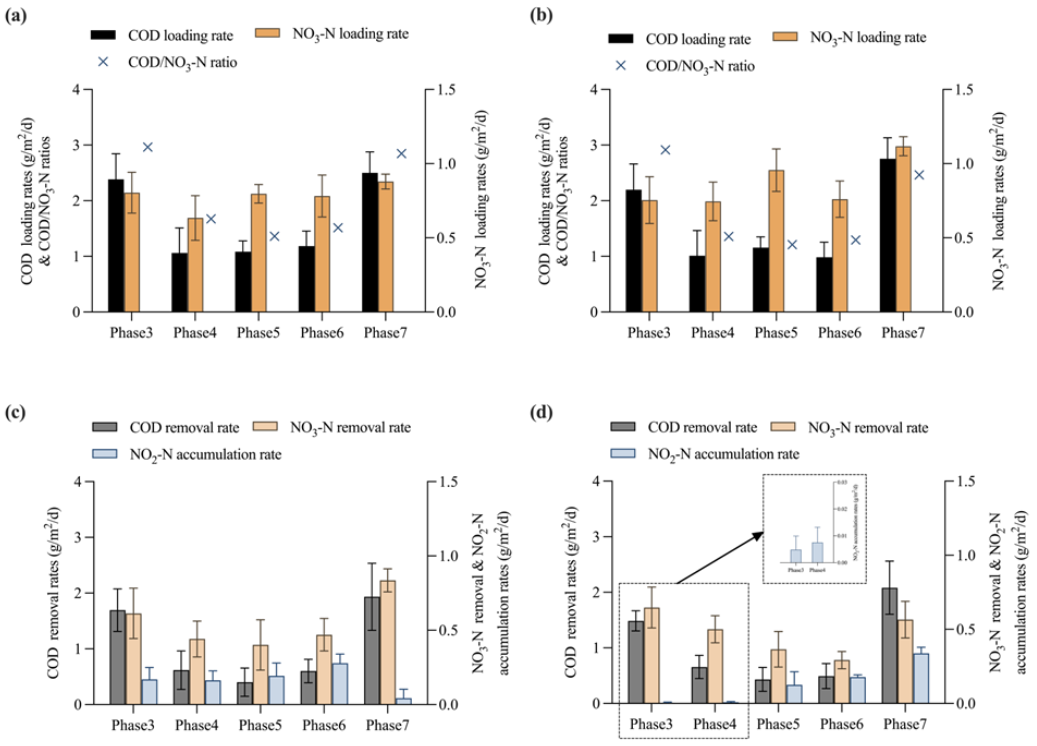

FIGURE 3: COD AND NO_3-N LOADING RATES WITH VARYING COD/N RATIOS IN (a) R1 (CONTROL) AND (b) R2 REACTORS; COD AND NO_3-N REMOVAL RATES, AND NO_2-N ACCUMULATION RATES IN (c) R1 (CONTROL) AND (d) R2 REACTORS, AT PHASES 3 TO 7

Throughout phases 3 to 5, as depicted in Figure 3c and Figure 4d, the carbon shifts coincided with a reduction in COD removal rates, from 1.49 ± 0.18 to 0.43 ± 0.21 g COD/m^2/d, due to the reduced COD loading (from 2.20 to 1.01 g COD/m^2/d) and COD/N ratio (from 3 to 1.5) as designed. The COD removal rate in phase 5 of the acetate-driven control reactor (R1), which was 0.40 ± 0.25 g/m^2/d, did not significantly differ from the methanol-fed reactor (R2).

3.2 Operational strategies for optimizing PDN biofilms: Balancing N2O emissions, mitigations and NO2 accumulation

Based on the dynamic and averaged values of off-gas emissions rates (CO_2 and N_2O-N) in both reactors, shown in Figures 4 and 5, this study evaluated the effect of scouring and varying COD/NO_3-N ratios on PDN performance and GHG emissions. The magnitude of average CO_2 emissions, ranging from 0.73 to 1.41 g CO_2/m^2/d, was much higher than emitted N_2O (0.001 to 0.05 g N_2O-N/m^2/d) in both PDN reactors. Significant N_2O emissions (0.22 to 14.44 g CO_2-equivalent/m^2/day) underscore the importance of optimizing operational conditions for mitigation. This is particularly important as the comparable levels of CO_2-equivalent emissions from N_2O and CO_2 in the PDN process, as shown in Figures 5c and 5d, highlight their similar impacts on atmospheric global warming.

As shown in Figure 3, with a limited electron donor (C/N=1.5) in phase 6, the averaged nitrate removal and nitrite accumulation in the non-scoured system (R1) were 0.47 ± 0.11 and 0.28 ± 0.06 g N/m^2/d, compared to 0.29 ± 0.06 and 0.18 ± 0.02 g N/m2/d for the scoured system (R2), respectively. The corresponding high N_2O emissions were 0.050 ± 0.017 and 0.053 ± 0.018 g N/m^2/d, respectively, corresponding to 12% and 18% of the removed nitrate (Figures 4 and 5). The latter NER was the highest emission rate observed in this study. The system with scouring released slightly more N_2O (5.51 g N_2O-N/m^3) per cubic meter of wastewater than the non-scouring system (5.17 g N_2O-N/m^3).

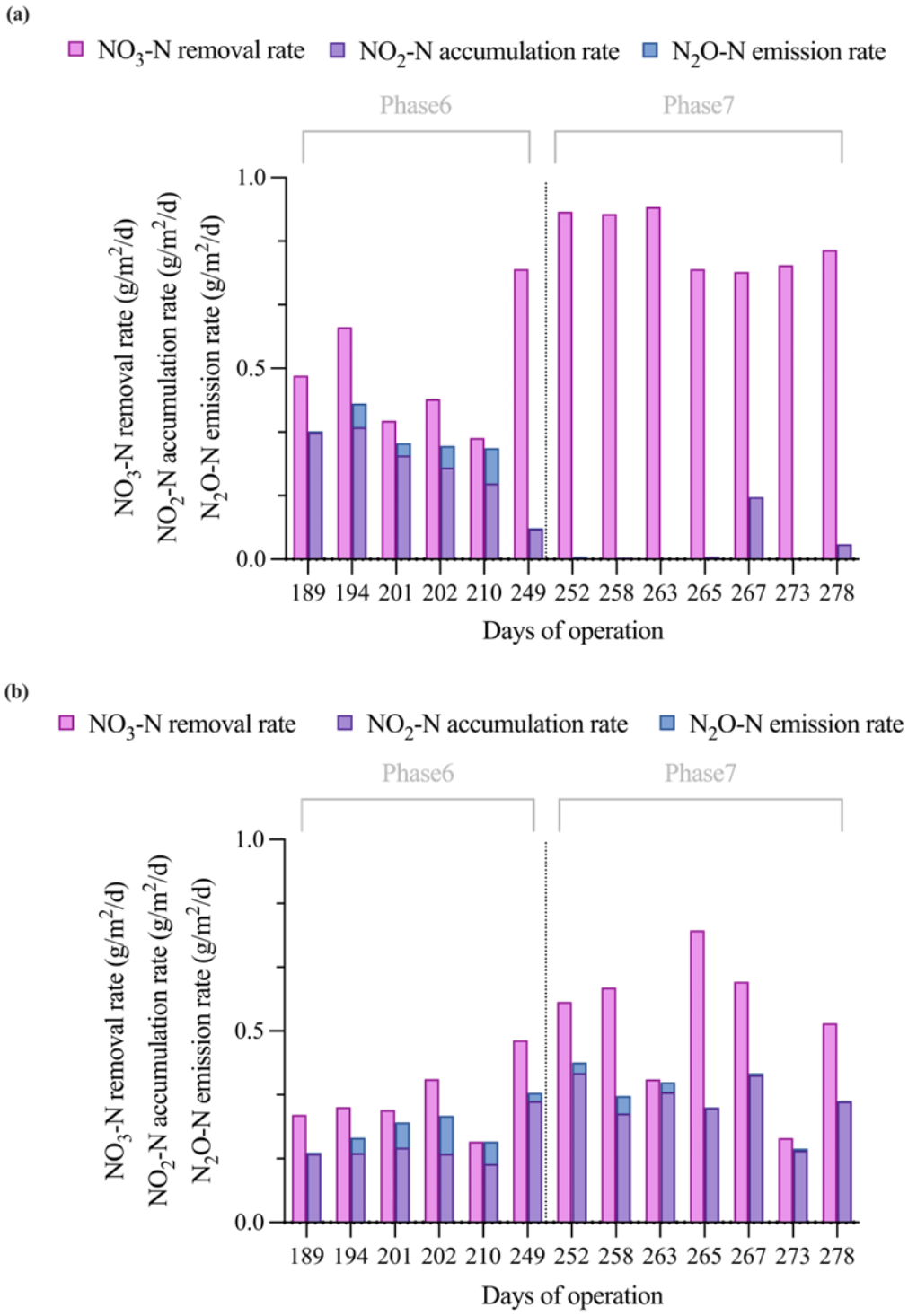

FIGURE 4: RATE VARIATIONS OF NITROGEN COMPOUNDS (NO_3-N, NO_2-N, N_2O-N) IN PHASE 6 (C/N=1.5) AND PHASE 7 (C/N=1.5) FOR REACTORS (a) R1 AS CONTROL AND (b) R2 WITH SCOURING

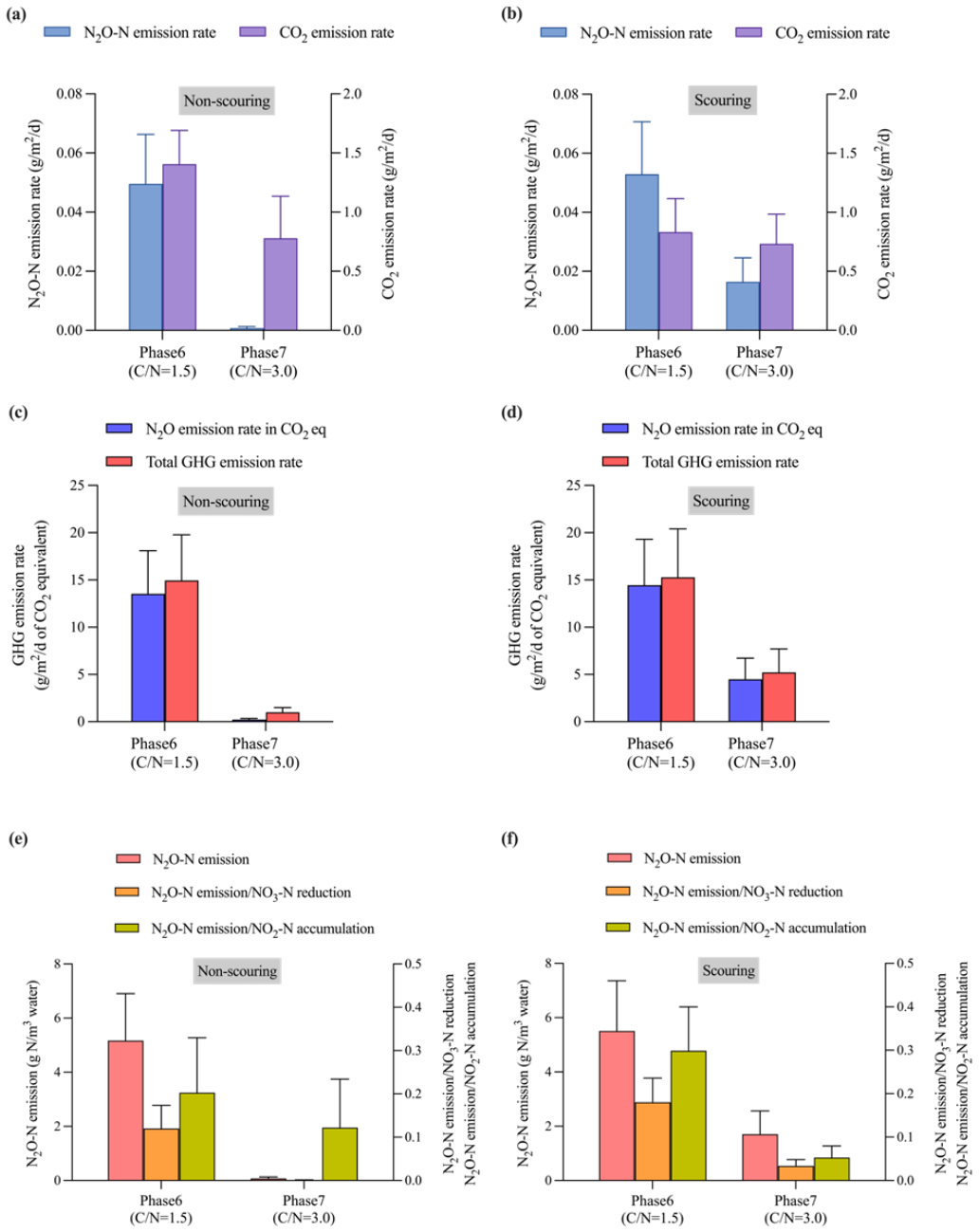

FIGURE 5: GREENHOUSE GAS (N_2O-N AND CO_2) EMISSION RATES AND RATIOS IN PHASE 6 (C/N=1.5) AND PHASE 7 (C/N=3) FOR REACTORS (a) (c) (e) R1 AS CONTROL AND (b) (d) (f) R2 WITH SCOURING

To date, no research has assessed the effects of scouring mode and COD/N ratio on N_2O emissions in the context of nitrite accumulation within immobilized biofilm systems, like rope-type media, for the partial denitrification process. Additionally, this study fills the research gap by identifying an optimal approach to balance and mitigate total GHG emissions in CO_2 equivalent while maximizing nitrite accumulation, thereby enhancing the efficiency and environmental sustainability of

the PDN process. In summary, the results showed the highest nitrate removal at a higher COD:N ratio of 3 compared to the ratio of 1.5, with scouring resulting in lower nitrate removal performance. However, the removed nitrate resulted in complete denitrification in non-scoured biofilms, showing achieving nitrite accumulation requires biofilm scouring, as suggested by Sun et al. (2024). Scoured biofilms emitted only 3% of the partially denitrified nitrate as N_2O but accumulated the highest nitrite-nitrogen ratio of 60%. Further mitigation of N_2O emission was feasible by increasing the COD: N ratio from 1.5 to 3. Comparing the systems at a COD: N ratio of 3, the non-scoured system showed the lowest N_2O emission (0.1% of NEE). The management of optimal COD/NO_3-N ratio and scouring stream is critical to mitigate N_2O emissions and TN removal in biofilm-based PDN systems.

4. CONCLUSIONS

This comprehensive study elucidated crucial insights into the PDN process in rope-type biofilm reactors, focusing on nitrite accumulation, N_2O emissions, and the influence of operational parameters. The nitrite accumulation rate peaked notably at 0.34 g N/m^2/d with the implementation of scouring for biofilm thickness control, accounting for 60% of denitrified NO_3-N, achieved with the increased HRT of 5 hours and COD/N ratio of 3. Furthermore, the research revealed that at a lower COD/N ratio and with scouring, the system showed N_2O emission breakthrough up to 0.053 g N/m^2/d (14.44 g CO_2 equivalent/m^2/d), demonstrating the significance of optimizing operational conditions to manage GHG emissions and nitrite accumulation in the biofilm PDN process. Additionally, the use of acetate as a carbon source proved significantly more effective than methanol for promoting nitrite accumulation. Furthermore, higher COD/N ratios of 3 effectively reduced N_2O emissions to 0.1-3% of the denitrified nitrate. These findings underscored the necessity of balancing carbon source selection and operational parameters to optimize PDN performance, reduce GHG emissions, and maximize nitrite accumulation in biofilm-based systems. This study lays the groundwork for advancing sustainable nitrogen management strategies in wastewater treatment.

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