

Evaluation of nitrous oxide gaseous emissions from a partial nitrification reactor operating under different conditions

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Abstract. In this study, continuous measurements of nitrous oxide gaseous emissions from a lab-scale partial nitrification (PN) chemostat treating ammonium-rich (1500 mgN/L) synthetic wastewater were performed, in order to achieve a deeper knowledge about its potential environmental impact. The reactor was operated at constant hydraulic retention time (HRT, 1 d) and nitrogen loading rate (NLR, 1500 mgN/L·d), with different influent alkalinity/nitrogen molar ratios (alk/N, 1 and 1.3) and dissolved oxygen concentrations (DO, 5.0, 3.0, 2.0, 1.5 and 1.0 mgO₂/L). As DO ranged between 5.0 and 1.5 mgO₂/L, the partial conversion of ammonium to nitrite was successfully achieved, with a negligible production of nitrate and nitrous oxide. When alk/N was increased from 1 to 1.3 (DO was not limiting, i.e. 2 mgO₂/L), the increase in ammonium-nitrogen removal rate (ANRR, from 717±17 to 945±21 mgNH₄-N/L·d) and the simultaneous decrease in specific N₂O-N production (from 0.33±0.01 to 0.23±0.01% of ANRR) were observed. When DO was set to 1.0 mgO₂/L, partial nitrification was irreversibly compromised, and a corresponding increase in specific N₂O-N production was observed (from 0.22±0.01 to 0.61±0.03% of ANRR). The results indicate a clear correlation between N₂O production and autotrophic ammonium to nitrite oxidation rate.

Keywords: alkalinity, ammonium, greenhouse gas emissions, nitrous oxide, partial nitrification

1. Introduction

For ammonium-rich effluents (NH₄-N > 500-1000 mg/L), conventional biological nitrogen removal processes based on nitrification and denitrification usually lack in terms of efficiency (high concentration of ammonium is toxic even for those microorganisms which are able to remove it) and cost-effectiveness. For such kind of effluents, the combination of partial nitrification (PN) and Anammox (Anaerobic Ammonium Oxidation) processes was proved to be an efficient and cost-effective solution (Van Hulle *et al.*, 2010; Zhao *et al.*, 2015), and it has been successfully applied to the treatment of reject water, landfill leachate, livestock manure and industrial wastewaters (Van Hulle *et al.*, 2010).

In recent years, assessment of greenhouse gas (GHG) emissions from wastewater treatment plants (WWTPs) is of growing concern; in particular, research focused on nitrous oxide (N₂O) production from biological nitrogen removal processes. According to the intergovernmental panel on climate change (IPCC, 2013), N₂O has a strong ozone layer depleting potential, and the third largest radiative forcing (i.e., the capacity of a gas to affect the balance between incoming solar radiation and outgoing infrared radiation, thereby contributing to climate change) among the anthropogenic gases in 2011, with an estimated lifetime of 131 years and a global warming potential 264-298 fold higher than CO₂. Thus, although the emission of nitrous oxide from WWTPs is relatively small (3% of the estimated total anthropogenic N₂O emission), it represents a significant factor (26%) in the greenhouse gas footprint of the total water chain (Kampschreur *et al.*, 2009). Law *et al.* (2012a) reported two key metabolic pathways involved in N₂O production by autotrophic ammonia oxidizing bacteria (AOB): autotrophic ammonia oxidation, where N₂O can be formed as a side product during the conversion of the ammonium-oxidation intermediate hydroxylamine (NH₂OH) to nitrite; and nitrifier denitrification (i.e. the reduction of NO₂ to NO and N₂O by autotrophic AOB).

Since nitrite is reported to trigger nitrous oxide production (Kampschreur *et al.*, 2009), shortcut nitrogen removal via the nitrite pathway is likely a major contributor to overall N₂O emission (Kinh *et al.*, 2017). In this study, gaseous N₂O emissions from a lab-scale partial nitrification reactor treating ammonium-rich synthetic wastewater were measured, with different operating conditions, in order to strike the right balance between overall process performance and GHG emissions.

2. Materials and methods

a. Reactor setup and operation

The PN (Sharon) unit consisted in a 2 L continuous flow stirred tank reactor operated as a chemostat (without biomass recirculation). A thermostatic bath was used to control temperature at 35±0.5°C; pH was constantly monitored and kept within the range 6.0-7.5 by dosing acid

(H₂SO₄ 1M) or base (NaOH 1M) solutions via peristaltic pumps.

During the experiments, dissolved oxygen concentration (DO) was continuously monitored and controlled; a variable mixture of air and dinitrogen gas was supplied at constant rate (1 L/min) in order to achieve different DO levels in the bulk liquid.

The reactor was inoculated with activated sludge drawn from the municipal wastewater treatment plant of Cagliari (Italy), fed with a synthetic medium with a NH₄-N concentration of 1500 mg/L, and operated for four months before carrying out the experiments described in this study. Influent flow rate was kept at 1.4 mL/min, resulting in a hydraulic retention time (HRT) and a corresponding sludge retention time (SRT) of 1 d. Total nitrogen loading rate (NLR) was equal to 1.5 gN/L·d. During the experiment, the influent alkalinity/ammonium nitrogen ratio (Alk/N) was changed from 1 to 1.3, resulting in a supplementary addition of bicarbonate in the medium. The final composition of the synthetic medium was: NH₄HCO₃ 8466 mg/L, KH₂PO₄ 1000 mg/L, MgSO₄ 100 mg/L, NaHCO₃ 0-2700 mg/L, and 10 mL/L trace elements solution as described in Milia *et al.* (2015). The resulting pH was 7.8-8.0.

The plan of the experimental activity is summarized in Table 1.

b. Analytical procedures

Influent and effluent ammonium (as NH₄-N) concentration was determined according to Standard Methods (APHA, 2005), using a Hitachi U-2000 spectrophotometer at a wavelength of 420 nm. The concentration of NO₂-N and NO₃-N was determined by ion-chromatography using a DIONEX ICS-90 equipped with an AS14A Ion-PAC 5 μm column. All samples were filtered (0.45 μm) before analyses, which were performed in triplicate. Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) concentrations were determined according to Standard Methods (APHA, 2005).

During nitrous oxide emissions measurement campaigns, headspace gas was collected from the reactor at constant flow rate (1 L/min), sent to a gas conditioning system (Bühler TGAK 3) and then to a Servomex 4100 gas

analyzer, where continuous measurement of N₂O concentration, expressed as ppmv, was performed via infra-red gas-filter correlation. Measurement campaigns lasted from 13 to 24 h; data from Servomex 4100 were logged (60 samples/h). Correspondingly, liquid samples from the mixed liquor were collected at the beginning and at the end of each campaign, in order to determine ammonium, nitrite and nitrate concentrations. The N₂O-nitrogen emission rate (ER) was calculated according to Lv *et al.* (2016) with some modifications:

$$ER = c \cdot Q \cdot p \cdot M_N \cdot 2 / (1000 \cdot R \cdot T \cdot V_L)$$

where ER is N₂O-N emission rate (mgN/L·d), *c* is the N₂O level in the gas sample (ppmv), *Q* is the volumetric flow rate of the off-gas (L/d), *p* is the atmospheric pressure (1 atm), *M_N* is the molar mass of nitrogen (g/mol), *R* is the gas constant (0.082056 L·atm/mol·K), *T* is the temperature (293.15 K) and *V_L* is the working volume of the reactor (2 L). Specific N₂O-N production was then calculated by dividing ER by the corresponding average ammonium nitrogen removal rate (ANRR, mgN/L·d).

Table 1. Plan of the experimental activity.

Phase	Duration (d)	DO (mgO ₂ /L)	Alk/N (-)
1	34	5.0	1.0
2	16	3.0	1.0
3	17	2.0	1.0
4	15	2.0	1.3
5	18	1.5	1.3
6	6	1.0	1.3

3. Results and discussion

a. Reactor performance

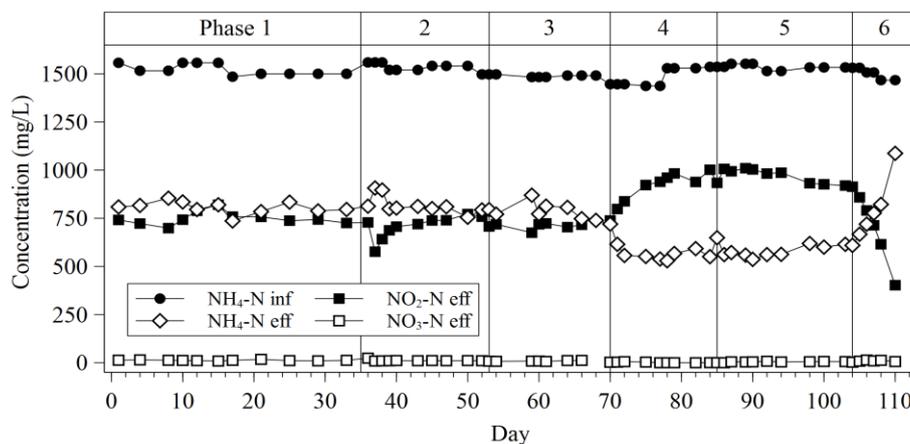


Figure 1. Process performance during the whole experimental period.

As shown in Figure 1, reactor performance was stable during Phase 1. Given the influent Alk/N ratio of 1.0 (Phase 1, 2 and 3), the decrease in DO down to 2 mgO₂/L did not affect overall process performance significantly. As reported in Table 2, negligible variations in process performance were detected among the first three experimental Phases: on days 1-69, ammonium conversion efficiency and effluent nitrite-to-ammonium molar ratio average values were 47±3% and 0.9±0.1, respectively. Such values were found to be slightly lower than expected, according to process stoichiometry (i.e., 50% and 1.0, respectively) (Van Hulle *et al.*, 2005). As suggested by Van Hulle *et al.* (2005), a mild limiting effect on AOB cell growth was likely caused by the short applied HRT, as confirmed by the relatively low biomass concentration achieved in the Sharon reactor (Table 2). As for other possible inhibiting factors, an excess of free ammonia and free nitrous acid, or a lack of inorganic carbon can be reasonably excluded, since they were outside the ranges considered as inhibiting by Van Hulle *et al.* (2007) and Guisasola *et al.* (2007).

Starting from day 70, increasing the Alk/N molar ratio up to 1.3 led to a corresponding increase in both NH₄-N removal efficiency (from 47±3 to 61±5%) and effluent NO₂/NH₄ molar ratio (from 0.9±0.1 to 1.6±0.3), compared to previous Phases. Such good process performance was maintained even when DO was reduced to 1.5 ppm (Phase 5), indicating no limiting conditions even below the dissolved oxygen concentration usually adopted in conventional wastewater treatment plants. Further decrease in DO (1.0 mgO₂/L, Phase 6) led to a quick and irreversible worsening of process performance (Figure 1), with the almost complete biomass washout. Such behavior was in agreement with those reported in previous studies: Guisasola *et al.* (2005) indicated an oxygen affinity

constant for autotrophic ammonium oxidation within the range 0.16-2.0 mgO₂/L; Van Hulle *et al.* (2007) determined an oxygen affinity constant of 0.94 mgO₂/L, and observed a detrimental effect of DO lower than 3 mgO₂/L in a Sharon reactor operating at 25°C and HRT=1.54 d; more recently, partial nitrification SBRs were successfully operated at DO even lower than 1 mgO₂/L (Ju *et al.*, 2015; Lv *et al.*, 2016).

b. N₂O emissions

Nitrous oxide measurement campaigns were carried out during each experimental phase, as stable conditions were confirmed, with the only exception of Phase 6, where stable performance could not be achieved: in that Phase, N₂O monitoring was performed on day 106. Results are shown in Figure 2.

Continuous mixing and aeration avoided N₂O accumulation in the bulk liquid. When stable performance was observed (Phases 1-5), N₂O emissions in the off-gas were always very low (average N₂O concentrations and ER ranged between 2.5-3.2 ppmv and 2.1-2.7 mgN/L·d, respectively), regardless of the applied DO (Figure 2a). Coherently, the increase in ammonium-nitrogen removal rate due to the higher applied Alk/N (Phases 4-5) was accompanied by a significant reduction of the specific N₂O-N production, i.e. from 0.35% (Phases 1-3) to 0.23% (Phases 4-5) of ANRR (Figure 2b).

During Phase 6, the irreversible worsening of process performance also led to a corresponding increase in N₂O gaseous emissions (up to 0.61% of ANRR). Such behavior can be justified by an increase in anoxic formation of N₂O (i.e. nitrifier denitrification) related to the shortage of available oxygen, which has been recognized as the main pathway contributing to N₂O production (Law *et al.*, 2012a). On the other hand, Law *et al.* (2012b) proved that an opposite behavior (i.e., the decrease in N₂O production with decreasing DO) can be observed in AOB cultures adapted to high levels of NH₄-N and NO₂-N (500 mgN/L) and low DO (0.5-0.8 mgO₂/L).

A wide range of nitrous oxide production rates in biological nitrogen removal processes were assessed referring to different system configurations (chemostat, continuous flow stirred tank reactor, sequencing batch reactor), size (lab-scale, pilot plant, full-scale plant) and operating conditions (Kampschreur *et al.*, 2008, 2009; Ali *et al.*, 2016). De Graaff *et al.* (2010) treated the liquid effluent of a UASB reactor using a continuous flow reactor without biomass retention, with a DO above 2 mgO₂/L, and detected a N₂O production ranging between 0.6 and 2.6% of total nitrogen load (0.14-0.30% in this study); Law *et al.* (2011) determined an average emission factor of 1.0±0.1% of total ammonium converted in a PN-SBR operating under different conditions; a lab-scale PN-SBR was studied by Rathnayake *et al.* (2013), who reported quite variable nitrous oxide productions, averaged out at 1.5±0.8% of the converted ammonium; Pijuan *et al.* (2013) studied the effect of different DO on N₂O emissions from a continuous pilot-scale granular airlift reactor performing both full and partial nitrification: the lowest emission factor (2.2% of total nitrified ammonium) was measured at DO of

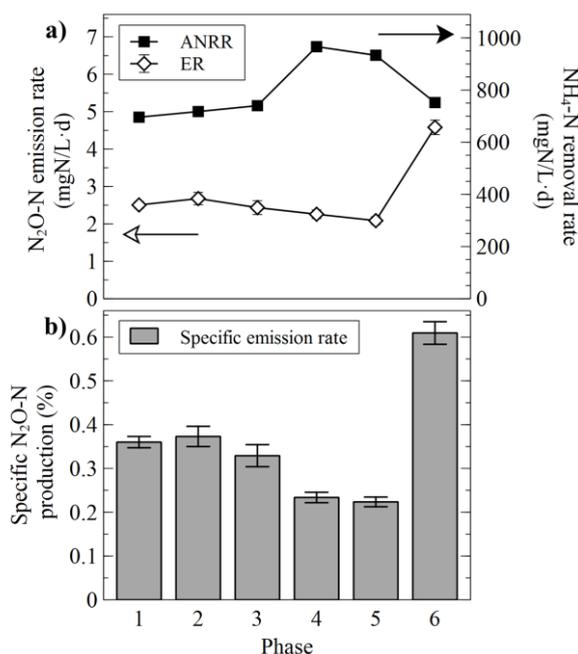


Figure 2. Results of nitrous oxide measurement campaigns.

Table 2. Average values of process parameters observed during stable experimental Phases (Phase 6 is excluded).

Phase	Influent NH ₄ -N (mg/L)	Effluent NH ₄ -N (mg/L)	Effluent NO ₂ -N (mg/L)	Effluent NO ₃ -N (mg/L)	NH ₄ conversion efficiency (%)	Effluent NO ₂ /NH ₄ ratio (-)	Biomass concentration (mgVSS/L)
1	1522±29	806±32	749±33	12±2	47±2	0.9±0.1	157±47
2	1536±21	819±47	707±59	12±4	47±3	0.9±0.1	134±26
3	1490±6	789±42	709±16	9±2	47±3	0.9±0.1	135±25
4	1482±47	580±59	902±90	2±2	61±5	1.6±0.3	177±16
5	1535±13	598±59	953±64	4±2	61±4	1.6±0.2	198±25

4.5 mgO₂/L or higher (when DO was reduced, a proportional increase of N₂O emission factor was observed, up to 6% of nitrified ammonium); a similar behavior was reported by Lv *et al.* (2016) who achieved stable partial nitrification in a SBR operating at oxygen-limiting conditions (DO = 0.35-0.85 mg/L), and measured nitrous oxide emissions ranging from 0.47 to 3.94% of total influent nitrogen; Kinh *et al.* (2017) reported a specific N₂O emission factor of 0.11-0.90% of oxidized ammonium nitrogen load in a partial nitrification SBR fed with a synthetic influent.

The results achieved in this study point at nitrifier denitrification as the main contributor to N₂O production. In this sense, the minimization of anoxic conditions in the lab-scale reactor due to continuous mixing and aeration may have led to the lower observed specific N₂O emissions, compared with most of the values reported in literature.

4. Conclusions

In this study, N₂O gaseous emissions from a Sharon reactor fed with a synthetic medium, and operated at different Alk/N (1.0-1.3) and DO (5-1.0 mgO₂/L), were monitored. When DO was not limiting, stable process performance was achieved, and N₂O emissions in the off-gas were lower than most of those reported in previous studies. The increase in influent Alk/N led to the increase in ANRR, which was accompanied by a significant reduction of the specific N₂O-N production. As DO was set at its lowest value, overall process performance was irreversibly compromised: beside the drop in ANRR, a corresponding increase in specific N₂O production was observed. Results suggest nitrifier denitrification as the main pathway contributing to N₂O production. GHG emissions from a partial nitrification reactor may be reduced by operating at low, as long as not process-limiting, dissolved oxygen concentrations.

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