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Nitrous oxide production in intermittently aerated Partial Nitritation-Anammox reactor: oxic N_2O production dominates and relates with ammonia removal rate

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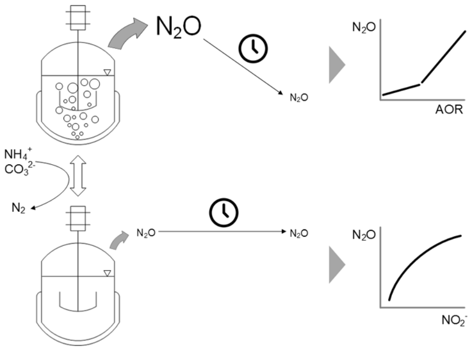
GRAPHICAL ABSTRACT



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ABSTRACT

Emissions of the greenhouse gas nitrous oxide from the Partial Nitritation-Anammox process are of concern and can determine the carbon footprint of the process. In order to reduce nitrous oxide emissions intermittent aeration regimes have been shown to be a promising mode of operation, possibly due to an effective control of accumulation of nitrogen intermediates. However, due to frequent changes of redox conditions under intermittent aeration regimes, nitrous oxide production and emissions are dynamic. In this study the production and emission dynamics of nitrous oxide in an intermittently aerated sequencing batch reactor were monitored in high temporal resolution, the contribution of different redox conditions to overall nitrous oxide production was quantified and the most relevant factors for nitrous oxide production were identified. The average fraction of nitrous oxide produced (per unit ammonium removed) was 1.1 ± 0.5%. Cycle-averaged approx. 80% of nitrous oxide was produced during aerated phases, the remaining 20% were produced during non-aerated phases. Yet, the intra-cycle dynamics of nitrous oxide were substantial. The net-production rate of nitrous oxide during aerated phases correlated with the ammonia removal rate, whereas the concentration of nitrite determined the production during non-aerated phases. While aerated phases contributed predominantly at the beginning of reactor cycles, non-aerated phases became the dominant source of nitrous oxide at the end. Particularly low net-production rates were observed at ammonia removal rates below 5 mg NH_3-N*gVSS^{-1}*L^{-1}, when the fraction of nitrous oxide produced was 0.011 ± 0.004% (per ammonia removed). Based on the nitrous oxide dynamics and

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correlations, reactor operation at relatively low nitrogen loadings (below 100 mg NH_4^+-N*L^{-1}), ammonia removal rates of approx. 5 mg NH_3-N*$gVSS^{-1}$*L^{-1} and nitrite concentrations below 1 mg NO_2^{-1}-N*L^{-1} appears as beneficial for low emission of nitrous oxide.

1. Introduction

The removal of ammonium (NH_4^+) from municipal wastewater streams is essential to protect receiving water bodies from eutrophication. One process to accomplish this task is the Partial Nitritation-Anammox (PNA) process [1]. To date, most PNA processes are applied in the treatment of NH_4^+-rich water streams at mesophilic temperatures (sidestream). Essentially, the PNA process consists of two biological conversion steps, a) Partial Nitritation (PN) and b) anaerobic ammonium oxidation (anammox). During PN NH_4^+ is converted aerobically to nitrite (NO_2^-) by ammonia oxidizing bacteria (AOB). During anammox NH_4^+ is, together with NO_2^-, converted anaerobically to the desired product dinitrogen gas (N_2) by anammox bacteria (AnAOB) [2]. PNA can be obtained via single-stage (one reactor) or two-stage (two reactors) operation. The majority (88% in 2014) of full-scale applications are single-stage systems in which AOB and AnAOB co-exist in bio-granules to metabolize NH_4^+ to environmentally inert dinitrogen gas (N_2) [1,3]. Both continuous and intermittent aeration strategies have been implemented in PNA systems to achieve efficient NH_4^+ removal [3]: While some studies show stable operation under continuous aeration [4], others find increased performance under intermittent aeration regimes and claim benefits of periodic anoxic phases for community metabolism, the suppression of undesired microbial groups (e.g. NOB) and energy savings due to a reduction of overall aeration time [5,6].

Emissions of nitrous oxide (N_2O) from PNA systems are of concern, as N_2O is an ozone depleting agent and a potent greenhouse gas with a global warming potential (GWP_{100}) of 298 [7]. Due to its large GWP_{100}, already low amounts of emitted N_2O can substantially contribute to the carbon footprint of PNA [8]. A better understanding of the biological turnover processes of nitrogen compounds during PNA and relevant parameters for the mitigation of N_2O emissions are needed to improve process sustainability.

Nitrous oxide originates mainly from three biochemical pathways during PNA [2,9–12]: 1) In the hydroxylamine oxidation pathway (HO), N_2O is produced by AOB during the oxidation of hydroxylamine (NH_2OH), 2) in the nitrifier denitrification (ND) pathway, N_2O is produced by AOB during the reduction of NO_2^-, and 3) during anaerobic reduction of NO_2^- and NO_3^- by heterotrophic denitrification (HD), N_2O is produced as an intermediate before the final reduction to N_2 [10]. N_2O produced during anammox is considered negligible [13].

The contribution of the different pathways to the total N_2O production depends on the activity of different microbial groups and varies with process conditions, e.g. concentration of NH_4^+, NO_2^-, DO and pH [2,14,15]. The production of N_2O by HO increases at high ammonia removal rates (AOR) and NH_4^+ concentrations [16], whereas N_2O production by ND is favored at high NO_2^- and low DO concentrations [14,17]. The availability of organic carbon is critical for the contribution of HD, and HD can become the dominant N_2O production pathway under stoichiometric sub-optimal carbon loadings [11].

Dynamics of N_2O production in PNA systems have been investigated in intermittently aerated and continuously-fed reactors [4,18] and also in continuously aerated sequencing batch reactors (SBRs) [8,19]. Yet, few studies have investigated the dynamics of N_2O production in intermittently aerated SBRs, which potentially combine the advantages of SBRs, e.g. high volumetric loading rates and low effluent concentrations, with advantages of intermittent aeration regimes, e.g. control of accumulation of N-intermediates and potential reduction of aeration energy [20,21]. In an earlier study, N_2O production was reduced in a PNA SBR at high frequencies of aeration intermittency [20]. The authors speculated that a decline in net-N_2O production rates at high aeration frequency was probably caused by lower transient NO_2^- accumulation and lower AORs. However, AORs were determined by extant AOB activity assays, which likely overestimated AOB activity.

This study monitored the AORs and N_2O dynamics of an intermittently aerated PNA SBR at a high temporal resolution. The combination of intermittent aeration and continuous stripping experiments together with N_2O micro-sensor measurements and off-gas N_2O analysis on a short time scale allowed a unique quantification of the contribution of different redox conditions to the overall N_2O production and enabled an in depth analysis of the effect of AORs and NO_2^- on net-N_2O production. To study the contribution of different redox conditions, AORs and NO_2^- concentrations we designed a series of experiments a) to identify the main phases of N_2O production during SBR cycles, b) to correlate the N_2O production with process parameters, c) to examine the effect of fluctuating pH as a driver for N_2O dynamics and d) to assess the potential contribution of heterotrophic bacteria to N_2O production.

2. Material and methods

2.1. Reactor operation

A 4L lab-scale reactor (Biostat A Plus, Sartorius, Göttingen, DE) was operated as an intermittently aerated sequencing batch reactor. Temperature was controlled at 30°C. The reactor was inoculated with biomass from a carrier based PNA pilot plant (AnoxKaldnes™, Sweden). Biomass was scraped off the carriers before transfer to the reactor. The reactor was fed with synthetic digester liquor medium, which was based on van de Graaf et al. [22] and contained per 1 L deionized water: 1694 mg NH_4HCO_3 (= 300 mg NH_4-N/L), 360 mg $NaHCO_3$ (CO_3^{2-}:NH_4^+ = 1.2), 170 mg KH_2PO_4 (1.25 mM), 750 mg $MgSO_4$*$7H_2O$ (3.05 mM), 450 mg $CaCl_2$*$2H_2O$ (3.07 mM), 10 mg $FeSO_4$*$7H_2O$ (36 µM), 10 mg EDTA (34 µM), 4 mg EDTA-Na_2 (11 µM), 0.43 mg $ZnSO_4$*$7H_2O$ (1.5 µM), 0.24 mg $CoCl_2$*$6H_2O$ (1 µM), 1 mg $MnCl_2$*$4H_2O$ (5 µM), 0.25 mg $CuSO_4$*$5H_2O$ (1 µM), 0.24 mg $NaMoO_4$*$2H_2O$ (1 µM), 0.19 mg $NiCl_2$*$6H_2O$ (0.80 µM), 0.2 mg $NaSeO_4$*$10H_2O$ (0.57 µM). The daily reactor load was 900 mg NH_4-N L^{-1} d^{-1}. One SBR cycle included a feeding phase (t_{feed}), reaction phase (t_{react}), settling phase (t_{settle}) and effluent phase ($t_{effluent}$) (nomenclature adapted from [23]). For experiments 1 and 3, a long cycle configuration was applied (Table 1). For experiment 2, a short cycle configuration was applied. The short cycle mimicked the last third of the long cycle operation. During t_{react} aeration was switched on and off 15 times (f_{redox} = 15) with each aerated and non-aerated phase lasting for 15 min. For the short cycle configuration, f_{redox} was 5. The length of aerated/non-aerated phases was fixed and guaranteed a full depletion of NO_2^- during non-aerated phases to prevent accumulation of NO_2^- over cycle time. Air was supplied at Q_{air} = 2.0 L min^{-1} during aerated phases through a diffuser at the bottom of the reactor. Stirring took place with 80 rpm during t_{feed} and t_{react} and was stopped during t_{settle} and $t_{effluent}$.

2.2. Process control & monitoring

The SBR was controlled by a digital control unit (Sartorius, Göttingen, DE), which itself was accessed by a customized LabView (National Instruments, Austin, US) protocol to manage cycle operation. Temperature, pH and DO were monitored continuously (every 10 s) using a Pt-100 temperature sensor, an EasyFerm plus K8 pH electrode