Chemical Engineering Journal 287 (2016) 269–276

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Effect of nitrite on the N_2O and NO production on the nitrification of low-strength ammonium wastewater

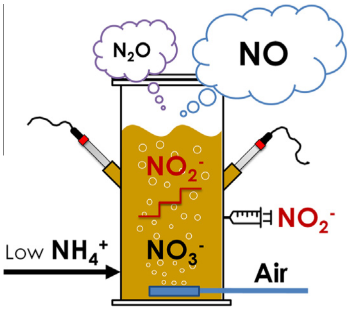
C.M. Castro-Barros [a], A. Rodríguez-Caballero [b], E.I.P. Volcke [a], M. Pijuan [b],*

[a] *Department of Biosystems Engineering, Ghent University, Coupure Links 653, 9000 Gent, Belgium*
[b] *Catalan Institute for Water Research (ICRA), Emili Grahit Street, 101, H_2O Building, Scientific and Technological Park of the University of Girona, 17003 Girona, Spain*

HIGHLIGHTS

- Nitrite effect on N_2O–NO emission in a low strength nitrifying system was studied.
- Nitrite presence in the reactor increases N_2O and NO emissions.
- High nitrite concentrations affect more NO emissions than N_2O emissions.
- The intermediate NO cannot be neglected during autotrophic denitrification.
- High nitrite concentrations inhibit the ammonium oxidising activity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 July 2015
Received in revised form 8 October 2015
Accepted 27 October 2015
Available online 18 November 2015

Keywords:
Low strength ammonium wastewater
Nitric oxide
Nitrifying system
Nitrite
Nitrous oxide

ABSTRACT

The effect of nitrite on N_2O and NO emission was assessed in a nitrifying lab-scale reactor fed with low strength ammonium wastewater. The effect of nitrite pulse additions (5–50 mg NO_2^--N L^{-1}) and of step-wisely increasing nitrite concentrations (0–150 mg NO_2^--N L^{-1}) was studied. For the pulse addition experiments, N_2O and NO emissions increased upon pulse addition of nitrite, decreasing to the original concentration once nitrite was consumed. The highest peak emissions were detected at nitrite concentrations of 50 mg NO_2^--N L^{-1}. For the step-wisely increasing nitrite tests, N_2O-N emission per NH_4^+-N converted increased linearly from 0.16% to 1.5%. NO emissions were substantially affected at nitrite concentrations higher than 50 mg NO_2^--N L^{-1}, reaching 3.8% NO-N per NH_4^+-N converted at 150 mg NO_2^--N L^{-1}. The results provide one of the first evidences of the combined effect of nitrite on N_2O and NO emissions, showing a stronger effect on NO emissions at high nitrite concentrations.

1. Introduction

Nitrogen removal during wastewater treatment emits nitrous oxide (N_2O) and nitric oxide (NO) [1,2]. N_2O is an important greenhouse gas with a global warming potential of 298-CO_2 equivalents [3], which may contribute significantly to the carbon footprint of wastewater treatment plants (WWTPs) [4,5]. NO is a very reactive gas that is involved in different physiological reactions in living organisms and becomes toxic at certain concentrations [6]. Both N_2O and NO contribute significantly to the ozone layer depletion [7,8]. The importance of studying the emissions of these gases from wastewater treatment lies on their environmental impact and their potential function as useful indicators of process disturbances [9]. Understanding the responsible mechanisms involved during the production of N_2O and NO, as well as knowing the factors that influence these emissions is essential to minimise their emissions and to reach a better process operation.

There is increasing evidence that the first step of nitrification (the conversion of ammonia to nitrite) conducted by ammonium

---

* Corresponding author. Tel.: +34 972 18 33 80.
E-mail address: mpijuan@icra.cat (M. Pijuan).

http://dx.doi.org/10.1016/j.cej.2015.10.121
1385-8947/

oxidising bacteria (AOB), is the major contributor to N_2O and NO emissions in the biologically mediated wastewater treatment processes [10,11]. AOB can produce N_2O and NO via two known pathways: the nitrifier denitrification and the hydroxylamine oxidation pathway. The first one is favored by limited oxygen conditions [12,13] and the presence of nitrite [1]. The second is enhanced at high ammonium oxidation rates [14]. Moreover, other factors such as pH [15], transient anoxic-aerobic conditions [16], salinity [17] or aeration intensity [18] have been reported to affect N_2O and NO emissions from nitrifying systems.

A lot of studies focused on the emissions of N_2O and NO for high strength ammonium wastewater, typically the reject water from the anaerobic digester [19–21]. The removal of nitrogen from such wastewater via nitrite has been gaining importance over the last years since it allows substantial energy (less aeration) and chemical savings compared to conventional processes over nitrate. However, partial nitrification systems used for the treatment of high strength wastewater have been shown to produce higher N_2O and NO emissions compared to full nitrification reactors [10,11] probably because of the high accumulation of nitrite in those systems and also the high ammonium conversion rates.

Relatively little research has been devoted to N_2O and NO emissions from systems treating low strength wastewater. Some studies focused on N_2O emissions from nitrification or combined nitrification–denitrification systems, without measuring NO [13,22]. Kampschreur et al. [23] is one of the few studies where NO was measured together with N_2O in a nitrifying culture. They found that N_2O and NO emissions are linearly proportional to the nitrite increase. In systems dealing with low-strength wastewater, the accumulation of nitrite may happen depending on the operating conditions and loading rates of the plant at certain moments. Occasional nitrite accumulation was also put forward as the cause for N_2O emissions from a full-scale municipal (low strength) wastewater treatment plant [24]. Moreover, the application of autotrophic nitrogen removal via nitrite for low strength ammonium wastewater is gaining interest since this technology can contribute to energy-positive WWTPs [25,26]. However, there is a lack of studies assessing the potential N_2O and NO emissions in these systems where nitrite can accumulate. Besides, the effect of nitrite on NO in nitrifying cultures adapted and non-adapted to nitrite is not well understood yet. Thus, further research is needed regarding the N_2O and NO emissions during nitrification of domestic wastewater and the effect of nitrite accumulation on the N_2O and NO emissions in these systems.

The present study explores the effect of nitrite on the N_2O and NO emissions during the full-nitrification of low strength synthetic ammonium wastewater through dedicated experiments. The effect of nitrite shocks as well as step-wisely increasing nitrite concentrations in the reactor on the emissions of both gases was assessed to gain understanding of the mechanisms producing N_2O and NO and to fully capture the overall emission dynamics of both gases. The results thus contribute to the potential reduction of their emissions during municipal wastewater treatment with punctual nitrite accumulation.

2. Materials and methods

2.1. Reactor operation

A sequencing batch reactor (SBR) of 8 L was inoculated with activated sludge from the municipal WWTP of Girona (Spain) and was operated during 5 months, obtaining a nitrifying mixed bacterial culture. The SBR was operated in 6-h cycles: 240 min of continuous feeding and aeration, settling during 100 min and 20 min for decanting. Four litres of synthetic wastewater were fed in each cycle, resulting in a hydraulic retention time (HRT) of 12 h. The influent ammonium concentration was set low (50 mg NH_4^+-N L^{-1}) and no temperature control was established in the reactor. Dissolved oxygen (DO) was controlled with a programmable logic controller (PLC) between 2.0 and 2.5 mg O_2 L^{-1} by adjusting the amount of air and nitrogen in the added gas stream, of which the total flow was kept constant at 3.5 L min^{-1}. The pH was controlled between 6.7 and 7.0 by adding 1 M $NaHCO_3$.

The composition of the synthetic wastewater used as influent consisted of: 282.1 mg NH_4HCO_3 L^{-1}, 87.8 mg KH_2PO_4 L^{-1}, 110.0 mg K_2HPO_4 L^{-1} and 2 mL L^{-1} of a trace element solution that included (g L^{-1}): 1.25 EDTA, 0.55 $ZnSO_4 \cdot 7H_2O$, 0.40 $CoCl_2 \cdot 6H_2O$, 1.27 $MnCl_2 \cdot 4H_2O$, 0.40 $CuSO_4 \cdot 5H_2O$, 0.05 $Na_2MoO_4 \cdot 2H_2O$, 1.37 $CaCl_2 \cdot 2H_2O$, 1.25 $FeCl_3 \cdot 6H_2O$, 44.4 $MgSO_4 \cdot 7H_2O$.

The batch tests were conducted when the reactor had been operating for 4 months and it showed stable operation, with all the ammonium from the influent converted to nitrate without accumulation of nitrite (detailed cycle analysis and nitrogen balance presented in Section S1 from Supplementary information).

2.2. Analysis and measurements

Cycle studies were carried out on a weekly basis to assess the reactor performance. Samples were taken along the cycle and immediately filtered through disposable Millipore filter units (0.22 μm pore size) and then analysed to determine the NH_4^+-N, NO_2^--N and NO_3^--N concentrations by ion chromatography (ICS5000, DIONEX). Mixed liquor suspended solids (MLSS) and volatile MLSS (MLVSS) were determined according to the standard methods [27]. During the batch tests the averaged MLSS and MLVSS in the reactor were 0.63 ± 0.09 g MLSS L^{-1} and 0.50 ± 0.05 g MLVSS L^{-1}, respectively.

N_2O and NO were monitored online in the gas phase every 5 s during the batch tests. N_2O was analysed with the infrared gas analyser Servomex 4900 (Servomex Group Ltd. East Sussex, UK) and NO was measured via the chemiluminescence gas analyser CLD64 (Eco Physics. Dürnten, Switzerland).

2.3. Batch tests

All batch tests were conducted in the SBR. After the decanting phase of the cycle previous to the batch test, the feeding pump was disconnected and the desired addition of ammonium and/or nitrite started. The pH and DO were kept at the same levels as normal reactor operation (described in Section 2.1). After each test, the SBR operation was kept normal at least for 24 h before another test was conducted.

2.3.1. Intermittent ammonium feeding with nitrite pulse additions

An experiment was designed to assess the effect of nitrite on N_2O–NO emissions in the absence of ammonium oxidation. A pulse of nitrite of 10 mg NO_2^--N L^{-1} (reactor concentration) was added without ammonium feeding. Once nitrite was completely oxidised to nitrate, ammonium feeding was re-established at a rate of 0.833 mg NH_4^+-N min^{-1}. This test was repeated twice.

2.3.2. Continuous ammonium feeding with nitrite pulse addition

Four sets of tests were conducted to check the effect of 4 different nitrite concentrations (5, 10, 25 and 50 mg NO_2^--N L^{-1}), added as pulses, on N_2O–NO emissions. During all the tests, ammonium was fed continuously at a rate of 0.833 mg NH_4^+-N min^{-1} and 3–4 pulses of nitrite (to provide the desired concentration of NO_2^--N L^{-1} in the reactor, see Table 1) were added.