Potential of nitrous oxide recovery from an aerobic/oxic/anoxic SBR process

Jianqiang Zhao, Nan Huang, Bo Hu, Luwei Jia and Guanghuan Ge

ABSTRACT

A single sequencing batch reactor (SBR) with an operating mode of anaerobic/oxic/anoxic (A/O/A) was developed to determine a simpler process to recover nitrous oxide (N_2O) from synthetic wastewater containing ammonia and glucose. This SBR system was initiated in A/O mode to implement nitritation (ammonia to nitrite) and then switched to A/O/A mode. Using measurements of the dissolved N_2O concentration and release rate, the total production and conversion rate of N_2O were calculated to reveal the potential of producing and recovering N_2O in the extended anoxic phase. Results showed that the A/O/A SBR could convert the majority of the nitrite available in the system into N_2O by heterotrophic denitritation over longer anoxic periods, and a conversion rate of 77% could be achieved. As a consequence, the A/O/A SBR presents potential ability to produce and recover N_2O from wastewater containing ammonia and organic carbon.

Key words | heterotrophic denitritation, nitritation, nitrous oxide, recovery, SBR

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INTRODUCTION

Nitrous oxide (N_2O), a potent greenhouse gas, can be emitted during wastewater treatment and significantly contributes to the greenhouse gas footprint (IPCC 2007). N_2O has been demonstrated to be produced and emitted in substantial amounts during nitrogen removal. A report provided by the United States Environmental Protection Agency revealed that the amount of N_2O emitted from wastewater treatment plants is 3% of the total global emissions of N_2O (USEPA 2006). In China, the amount of N_2O emitted from wastewater treatment plants is about 1,260 t(N) per year (Wang et al. 2014b). In recent years, a large amount of research has focused on the emission and control of N_2O during biological wastewater treatment (Kampschreur et al. 2009).

During biological wastewater treatment, processes such as autotrophic nitrification and heterotrophic denitrification, have been identified as major sources of N_2O (Wang et al. 2014a, b). Heterotrophic denitrification is well-known to play an important role in N_2O production from nitritation (ammonia to nitrite) reactors treating anaerobic sludge digestion liquor (Wang et al. 2014a). N_2O production and emission increase when oxygen is limited (Wunderlin et al. 2012), under low organic carbon concentrations (Schalk-Otte et al. 2000; Itokawa et al. 2001) and when the intracellular organic carbon PHB (poly-β-hydroxybutyrate) is used as the carbon sources for denitrification (Beun et al. 2000; Schneider et al. 2011; Jia et al. 2012).

Despite the environmental risks it produces, N_2O is also a type of resource that can be used as a powerful oxidant in combustion reactions in many situations (Scherson et al. 2013). If N_2O is recovered from biological sewage treatment plants, the release of N_2O to the atmosphere will be mitigated and the energy utilization efficiency of the wastewater treatment plant can be improved.

A N_2O recovery process called coupled aerobic–anoxic nitrous decomposition operation (CANDO) was reported to recover N_2O successfully through PHB denitrification (Scherson et al. 2013, 2014). The CANDO process is a two-stage sequencing batch reactor (SBR) process. Ammonia is converted into nitrite in the first SBR, and N_2O is recovered by PHB denitrification in the second SBR. N_2O can be used to improve combustion of methane, a product of anaerobic sludge digestion in biological wastewater treatment plants. In the second SBR, the conversion rates of nitrite to N_2O are 65% and 75–80% with the carbon sources of acetate and sludge hydrolysis-acidification liquor, respectively. Using N_2O to improve combustion, the output power of biogas power generation can increase by 5.7–7.3% (Scherson et al. 2013, 2014).

In China, sludge outputs from domestic wastewater treatment plants exceed 30 million tons per year. Over 50 plants use biogas produced in anaerobic sludge digestion for power generation or combustion. Recovery of N_2O from sludge liquor, digestion liquor and wastewater containing chemical oxygen demand (COD) and ammonia to improve biogas combustion is thus an interesting endeavour. In this paper, an anaerobic/oxic/anoxic (A/O/A) SBR process was developed to study the potential of N_2O recovery from synthetic wastewater containing COD and ammonia based on previous investigations of the impacts of heterotrophic denitrification on nitration. In contrast to the CANDO system proposed by Scherson *et al.* (2013, 2014), the proposed system allows N_2O recovery from a single SBR through nitration and denitration. The results obtained in this study help to improve the current understanding of the impacts of heterotrophic denitrification on N_2O production and further the development of a novel process for N_2O recovery from wastewater containing ammonia and COD.

MATERIALS AND METHODS

Laboratory-scale SBR

The laboratory-scale SBR had a height of 35 cm, inside diameter of 16 cm and working volume of 5,000 cm^3 and was operated in the laboratory. Compressed air was supplied to the reactor during the aerobic phase and the air-flow rate was adjusted to 40 L/h. To select a suitable aeration flow rate, rates of 20, 40, 60 and 80 L/h were tested. It was found that lower aeration flow rate correlated with higher nitrite accumulation ratio and longer nitration duration, whereas higher aeration flow rate correlated with lower nitrite accumulation ratio rate and shorter nitration duration. Therefore, a moderate aeration rate of 40 L/h was adopted in this study. The contents of the reactor were mixed using a mechanical stirrer at 60 rpm in all phases except for the settling and decanting phases. The mixed liquor temperature was controlled using a water jacket to $27 \pm 1 °C$. The influent and effluent were pumped and controlled by a microcomputer-controlled system.

Reactor start-up

The synthetic wastewater was composed of (per litre): 0.500 g $C_6H_{12}O_6$, 1.354 g NH_4HCO_3, 0.330 g KH_2PO_4, 0.050 g $MgSO_4 \cdot 7H_2O$, 0.016 g $CaCl_2$, 0.1500 g $NaHCO_3$ and 1 mL of a trace element stock solution (Lovley &

Phillips 1988) to achieve influent COD and NH_4^+-N concentrations of 530 mg/L and 240 mg/L, respectively.

The SBR was operated over one cycle of 8 h consisting of 5 min of anaerobic feeding, 5 h of anaerobic stirring, about 2 h of aerating (controlled by dissolved oxygen (DO) level) and 55 min of settling and decanting. No excess sludge discharged in the start-up period. In each cycle, 2 L of synthetic wastewater was fed to the reactor, resulting in a hydraulic retention time of 20 h.

The reactor was seeded with sludge from a domestic wastewater treatment plant in Xi'an, China. The preliminary concentration of the mixed-liquor suspended solids (MLSS) was 2,800 mg/L. After 20 d of nitrifying culture, 95% of the NH_4^+ was converted into NO_2^-; at this point, successful completion of startup was achieved.

Operating mode for N_2O recovery

After completion of SBR start-up, 4 months of stable nitration operation was carried out. The MLSS concentration reached $5,470 \pm 28$ mg/L. The operation mode of the SBR was then changed to N_2O recovery mode with one cycle of 24 h consisting of 5 min of anaerobic feeding, 3 h of anaerobic stirring, about 2 h of aerating (controlled by DO level), 18 h of anoxic stirring, 5 min of aerating to release N_2O and 50 min of settling and decanting. An extended anoxic period was designed to study the potential of N_2O production and recovery in the new operating mode.

Analytical methods

Ammonium (NH_4^+-N), nitrite (NO_2^--N), nitrate (NO_3^--N) and MLSS were analysed according to *Standard Methods* (APHA 1998). The pH in the reactor was measured with a pH meter (pH S10, Sichuan, China). DO concentrations in the reactor were monitored with a DO meter (Hach-HQ30d, USA). N_2O concentrations in the liquid phase were measured using a N_2O microsensor (Unisense, Denmark) with data logged every 10 s.

Calculations of N_2O production

N_2O release rate was defined as the amount of N_2O released per minute per litre of liquid. Total N_2O yield was defined as the total amount of N_2O produced per minute per litre of liquid. Zhang *et al.* (2012) and Quan *et al.* (2012) have shown that the profiles of air stripping rates of N_2O can be described using linear equations with respect to the

dissolved N_2O concentration in the liquid phase, as shown in Equation (1):

$$r_e = kC_{N_2O} \tag{1}$$

where r_e is the N_2O release rate in mg N_2O-N/(L·min), C_{N_2O} is the soluble N_2O concentration in mg N_2O-N /L, and k is the N_2O release coefficient in 1/min.

From r_e, the accumulated amount of N_2O released (mg N_2O-N/L) can be calculated by integrating r_e with the running time. Total N_2O production (mg N_2O-N/L) can be calculated by adding the accumulated amount of N_2O released with liquid concentrations of N_2O. The total N_2O yield, mg N_2O-N /(L·min) can be calculated by adding r_e to the variation rate of N_2O concentration in the liquid; the latter can be calculated from the measured values (Quan *et al.* 2012; Zhang *et al.* 2012).

N_2O release tests were conducted to determine the mass transfer coefficient, k, of Equation (1). The results revealed that the N_2O release rate is linearly correlated with liquid N_2O concentration with k being 0.144 /min ($R^2 = 0.9395$) for aeration of 40 L/h (including air stripping and diffusion by stirring at 60 rpm in aeration periods) and 0.0057 /min ($R^2 = 0.9858$) for stirring only (diffusion by stirring at 60 rpm during non-aeration periods).

RESULTS AND DISCUSSION

N_2O production in the nitration process

Liquid N_2O concentrations were measured, and the accumulated amount of N_2O released, total N_2O produced, release rate and total yield under aeration intensity of 40 L/h were calculated according to the methods described above; the results are shown in Figure 1(a). The corresponding concentrations of NO_2^-, NH_4^+, NO_3^- and DO, and pH values were measured and are shown in Figure 1(b).

During nitration, aeration flow of 40 L/h was supplied continuously until the DO concentration exceeded 1.0 mg/L, which signified the end of the nitration process. Most DO concentration values were 0.3–0.4 mg/L within the 1.8 h aeration period. pH dropped gradually from 8.1 at the beginning to 7.6 at the end. A NO_2^--N concentration of 71.0 mg/L was produced and about 82% of the ammonia nitrogen (86.4 mg/L) was converted. A total N_2O production of 9.6 mg/L was obtained, and the maximum total yield was 0.18 mg N_2O-N/(L·min) (Figure 1(a)). The N_2O conversion
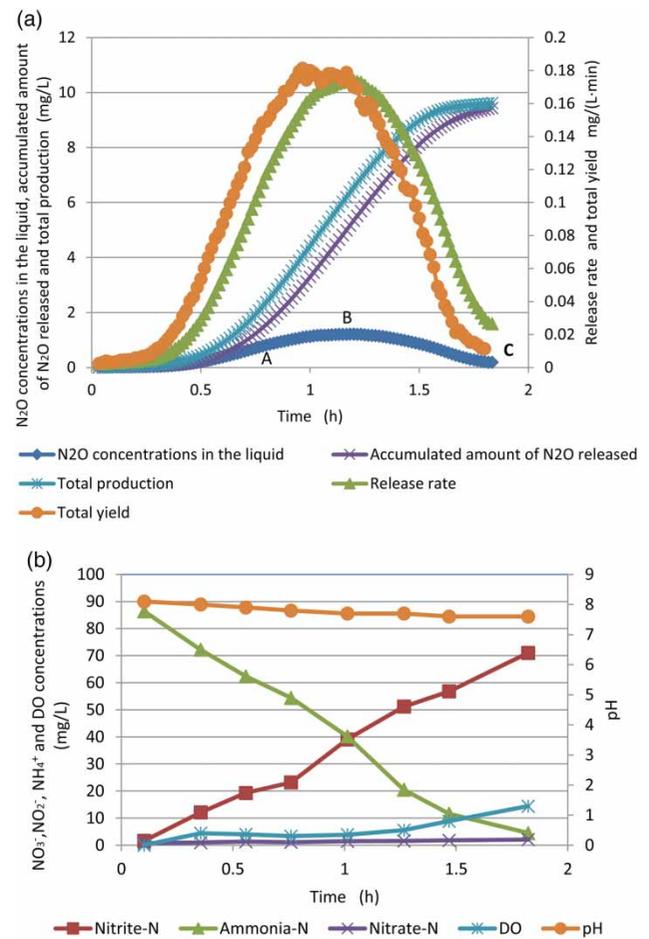

Figure 1 | Time profiles under aeration intensity of 40 L/h of: (a) N_2O concentrations in the liquid, accumulated amount of N_2O released, total production, release rate and total yield; (b): NO_2^-, NH_4^+, NO_3^-, and DO concentrations and pH values.

rates were about 86% of the total nitrogen removed and 11% of the ammonia nitrogen load. The vast majority of N_2O produced during nitration was released as a gas into the air; only a small amount of this compound remained in the liquid as a dissolved material.

Role of heterotrophic denitritation in N_2O production

To gain insights into the function of heterotrophic denitritation in N_2O production during the nitration process, duplicate tests were conducted to monitor liquid N_2O concentrations under the same conditions. Figures 2 and 3, respectively, show the curves of liquid N_2O concentration as a function of time when aeration is stopped at the rise period (marked by the arrow in Figure 2, corresponding to point A in Figure 1(a)) and the highest point (marked by the arrow in Figure 3, corresponding to point B in Figure 1(a)) of the liquid N_2O concentration.
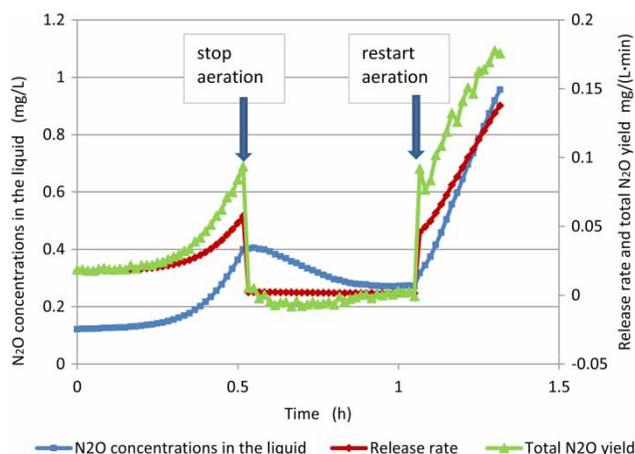
Figure 2 | Curves of N_2O concentrations in the liquid, release rate and total N_2O yield as a function of time when aeration is stopped in the rise period marked A in Figure 1(a).

The test results shown in Figure 2 reveal that the liquid N_2O concentration initially increases and then gradually decreases when aeration is stopped at the rise period. The early and brief increase in liquid N_2O concentration might be brought about by the decrease in air stripping. The subsequent gradual drop may be attributed to the concentrations of COD in the rise period remaining high enough to be used as the carbon source for reducing N_2O to N_2 by heterotrophic microbes. During this process, COD, NH_4^+ and NO_2^- concentrations changed from 108 mg/L, 84.3 mg/L and 0.6 mg/L to 93 mg/L, 72.0 mg/L and 12.0 mg/L, respectively. The negative value of total N_2O yield in Figure 2 demonstrates that N_2O was consumed. The reduction rates of NO and N_2O are greater than those of NO_3^- and NO_2^- during heterotrophic denitrification under normal conditions (Pan *et al.* 2012). Therefore, N_2O may be quickly restored into N_2 and appears to resist accumulation or release when the organic carbon was sufficient (Wang *et al.* 2014a, b).

Figure 3 reveals that liquid N_2O concentrations continuously increase when aeration is stopped at the highest point (point B in Figure 1(a)). The early, rapid and short increase in liquid N_2O concentration might be brought about by a decrease in air stripping. The subsequent continuous rise may be attributed to lower concentrations of COD at the highest point and intracellular carbon source used as the electron donor for reducing NO_2^- to N_2O by heterotrophic microbes; here COD, NH_4^+ and NO_2^- concentrations of 58 mg/L, 40 mg/L and 39 mg/L, respectively, were obtained. N_2O has been reported to accumulate in liquid when organic carbon is limited because of weak competition of N_2O reductase for electrons (Li *et al.* 2013). Similarly, when PHB is used as

the carbon source, N_2O emission increases because of slow PHB degradation (Jia *et al.* 2012).

In Figure 3, when aeration is stopped at the highest point (point B in Figure 1(a)), the total yield of N_2O is approximately 0.055 mg/(L·min); which is about 30% of the maximum value of the total yield during nitritation (Figure 1(a)). This finding demonstrates that the function of heterotrophic denitritation in N_2O production in the nitritation reactor is considerable, especially under lower DO concentrations and exhaustion of the available organic carbon.

## Production of N_2O by heterotrophic denitritation via the A/O/A SBR

According to the function of heterotrophic denitritation for N_2O production described above, an operation mode for N_2O recovery was carried out by extending the nitritation SBR to include a longer anoxic period (after aeration ceased at point C in Figure 1(a)). N_2O production in the initial nitritation period and by heterotrophic denitritation in the later anoxic period was observed, and results are shown in Figure 4. The concentrations of NH_4^+, NO_3^-, NO_2^- and DO and pH of the system were measured to determine key points, such as the lowest and highest points of the liquid N_2O concentration curve, as shown in Figure 5.

Test results showed that nearly all of the nitrite accumulated in the nitritation phase, 71.0 mg/L, was reduced after about 18 h in the anoxic phase with a total N_2O production of 54.6 mg/L, which is much greater than that for the nitritation phase (9.6 mg/L). The conversion rate of nitrite to N_2O obtained was 77%, higher than that obtained with acetate as the carbon source (65%) by Scherson *et al.* (2013, 2014). During the 2 weeks of continuous tests, MLSS of the reactor decreased slightly from 5,470 to 4,888 mg/L. The average specific N_2O production rate was 0.58 mg-N per g MLSS
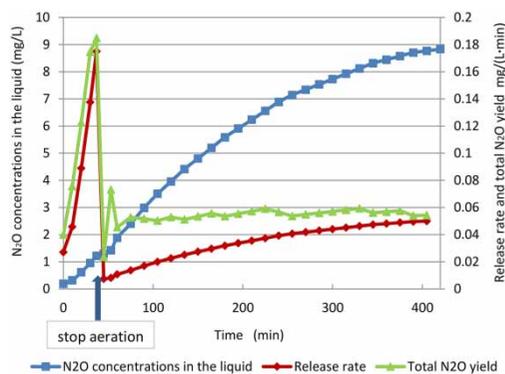
Figure 3 | Curves of N_2O concentrations in the liquid as a function of time when aeration is stopped at the highest point marked B in Figure 1(a).
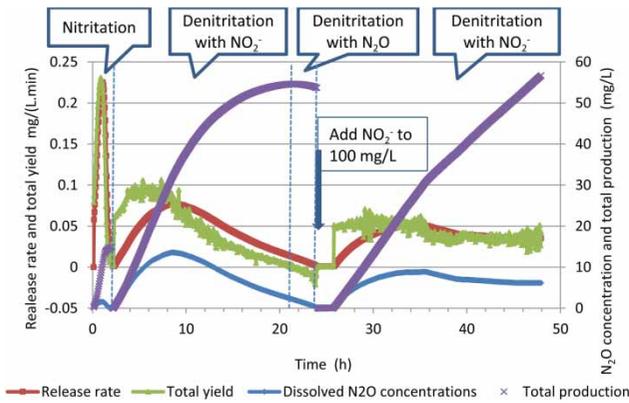
Figure 4 | Dissolved N_2O concentrations, total production, release rates and total yields obtained during the aeration and anoxic periods.
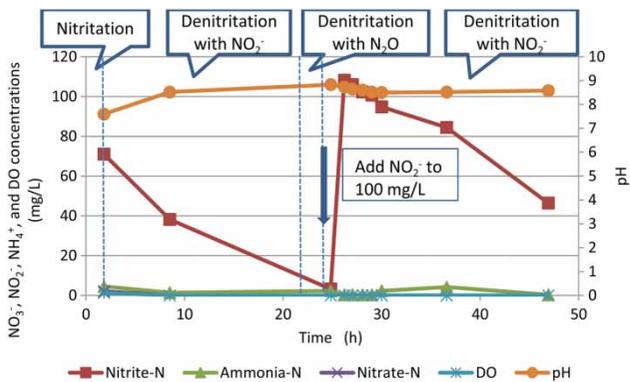
Figure 5 | pH values and NH_4^+, NO_3^-, NO_2^- and DO concentrations obtained during the aeration and anoxic periods.

per h in the later anoxic phase. However, the pH always increased from the beginning to the end of the later anoxic phase in one cycle, e.g. 7.60 to 8.83 as shown in Figure 5.

As shown in Figure 4, to investigate the potential of N_2O production in the anoxic phase by heterotrophic denitritation further, 100 mg/L NO_2^--N was added to the reactor when the liquid N_2O concentration was near zero (marked by the arrow in Figure 4). The liquid N_2O concentration, release rate, total yield and total production increased when additional nitrite nitrogen was supplied. These results indicate that the proposed operation mode could reduce most of the nitrite nitrogen remaining in the reactor after the aeration phase and convert it into N_2O. The high concentration N_2O in the liquid was easily recovered with brief additional aeration.

Figure 4 further shows that heterotrophic intracellular carbon source denitritation not only reduces nitrite nitrogen to N_2O but also reduces N_2O to N_2 when nitrite nitrogen is exhausted, as demonstrated by the negative values of the areas of total yield in Figure 4.

Impacts of influent COD concentrations to N_2O production by the A/O/A SBR

Theoretical reduction of NO_2^- to N_2O without cell synthesis required a COD/N ratio of 1.14. At lower COD/N ratios, insufficient organics was converted into PHB in the anaerobic and aerobic phases, and PHB was insufficient for reduction of nitrite; residual NO_2^- remained in solution at the end of the anoxic phase. In the study of Scherson *et al.* (2013, 2014), COD/N ratios of 1.5 and 3.0 were adopted. Therefore, besides the influent COD of 530 mg/L (COD/N is 2.2) mentioned above, two other concentrations of influent COD, namely 265 (COD/N is 1.1) and 1,060 mg/L (COD/N is 4.4), were selected to investigate their effects on N_2O production by heterotrophic denitritation in the later anoxic phase of the A/O/A SBR. Results showed that, when influent COD concentration was changed from 530 to 1,060 mg/L, the complete nitritation process needed double time to complete. However, the time for nitrite conversion to N_2O in the later anoxic phase was shortened for 2 h with a slight increase in total N_2O yield. Variation of pH and DO during the later anoxic phase were similar to that of COD, which was 530 mg/L. However, MLSS increased from the initial value of 4,888 to 5,166 mg/L at the end of the 1 week of continuous tests with an average specific N_2O production rate of 0.72 mg-N/g MLSS/h in the later anoxic phase. When influent COD concentration was switched to 265 mg/L, corresponding time for complete nitritation process were shortened only by about 15 min. The nitrite still remained in the reactor after 18 h of anoxic stirring, resulting in only 23.6 mg/L of nitrite being converted to N_2O. The variation of pH and DO followed the same trends as that of COD, which were 530 and 1,060 mg/L. However, MLSS decreased from the initial value of 5,166 to 4,785 mg/L at the end of the 1 week test. As a result, COD/NH_4^+-N was greater than 2.2 in the influent, and might be necessary for completely denitrifying nitrite to N_2O in the later anoxic phase.

Potential of energy recovery

N_2O can act as a powerful oxidant in combustion reactions. When used to oxidize methane, N_2O increases the heat of reaction by -329 kJ/mol compared with O_2 (Scherson *et al.* 2013). Injections of N_2O into a biogas-fed engine at flow rates simulating a full-scale system increased power output by $5.7 - 7.3\%$ (Scherson *et al.* 2014). Scherson *et al.* (2014) found that conversion of NO_2^- to N_2O was essentially complete within 24 h with an initial NO_2^- concentration of $75 - 85$ mg-N/L at the beginning of the anoxic phase. In

contrast, initial NO_2^- concentration of 65–76 mg-N/L at the beginning of the anoxic phase was essentially completely reduced in about 18 h of anoxic phase in our study. This indicates that a similar amount of potential energy as in Scherson et al. (2014) could be recovered and used for improving methane combustion. Thus, A/O/A SBR has the potential for production and recovery of N_2O from wastewater containing ammonia and organic carbon, such as reject water.

CONCLUSIONS

When the operating mode of the single SBR was A/O/A, the majority of the nitrite transformed from ammonia nitrogen during nitritation process could be converted into N_2O in the later anoxic period by heterotrophic denitritation with a conversion rate of 77%. As a consequence, the proposed mode can potentially recover N_2O from synthetic wastewater containing ammonia and glucose at influent ammonia nitrogen concentration of 240 mg/L and COD concentration between 503 and 1,060 mg/L, corresponding to COD to NH_4^+-N ratios greater than 2.2.

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