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A control system for nitrification / denitrification over nitrite in SBR with simultaneous mitigation of N₂O emissions.

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Abstract

A control system for limiting N₂O emissions in a SBR treating an ammonium rich effluent (~500 mgN.L⁻¹) with nitrification / denitrification over nitrite is presented. This system is based on the use of derivatives of DO and ORP signals for on line control of aerobic and anoxic periods. During the 120 days of operation, the effect of different operating conditions on N₂O emissions during nitrification has been analyzed. Experimental results have highlighted the effect on N₂O emissions of: HNO₂ concentration, DO concentration and the presence of COD during nitrification. The control system allows reducing the N₂O emission factor (N-N₂O per N removed) to less than 1%.

Keywords: SBR; Control; Nitrification; Denitrification; Nitrous oxide.

Introduction

Nitrification combined with denitrification (N/DN) over nitrite is an interesting process for biological treatment of ammonium-rich wastewaters. In this system the needs of oxygen and organic matter are lower than those of conventional biological nitrification and denitrification. This alternative allows reducing energy consumption and chemical use for denitrification (example: methanol).

However, in system treating N-rich wastewater, ammonium-oxidizing bacteria (AOB) can produce a significant amount of N₂O which is a major greenhouse gas. It was demonstrated that a major part of this gas was produced by the mechanism of autotrophic denitrification, i.e. the reduction of nitrite by AOB (Kampschreur et al., 2009). The N₂O emissions of systems with N/DN over nitrite can be much higher than those of conventional system with full nitrification (Rodriguez-Caballero et al., 2013). In Sequencing Batch Reactor (SBR) operated for N/DN over nitrite, N₂O emission factors can reach more than 5% (mass of N-N₂O produced per N removed) which clearly counter balances the benefits of partial nitrification, i.e. reduction of oxygen demand and COD needs (Rodriguez-Caballero et al., 2013). Moreover, alternating aerobic and anoxic periods has also a detrimental effect on N₂O emissions (Rodriguez-Caballero and Pijuan, 2013).

Therefore the objective of this work is to develop a control system for N/DN over nitrite with simultaneous mitigation of N₂O production. Compared to previous systems based on on-line nitrite measurement (Lemaire et al., 2011), this controller is based on simple sensors, cheap and easy to maintain: dissolved oxygen (DO) and Oxidation-Reduction Potential (ORP).

Material and Methods

Experimental set-up and operating conditions

Experiments were performed in a lab-scale reactor (1.43-1.63 L of liquid) equipped with an intermittent aeration system (fine bubble injection), a mechanical stirrer (Rushton type with constant stirring rate of 465 rpm) and a water jacket for temperature control (maintained at 28 ± 0.5 °C). pH (H8481HD from Schott), dissolved oxygen (DO) (Visiferm DO Arc 120 from Hamilton) and oxidation-reduction potential (ORP) (PL89225Pt from Schott) were monitored

during all the study. Air flow rate was imposed with a mass flowmeter. The gas was collected at the top of the reactor with a flow of $0.2 \text{ L}\cdot\text{min}^{-1}$ for analysis of N_2O (X-STREAM X2GP from Emerson; range: 0-100 ppm). All the data were monitored every 20 seconds. A control panel connected to a computer allowed managing stirring, aeration and all inputs and outputs of the reactor. The system was inoculated with a sludge sample from the activated sludge process of a WWTP with stable nitrification (Graulhet, France, 50 000 PE; sludge retention time of 20 d) receiving domestic and industrial wastewater (70% from tanneries). The initial concentration was closed to $4 \text{ gVSS}\cdot\text{L}^{-1}$. The lab scale reactor was operated in SBR mode with automatic feeding and wastage. A sludge retention time (SRT) of 15 d^{-1} was maintained. The system was fed with a high strength synthetic wastewater ($462 \text{ mgN-NH}_4^+\cdot\text{L}^{-1}$) and a complementary solution was used as a source of organic carbon ($18.8 \text{ gCOD}\cdot\text{L}^{-1}$) for heterotrophic denitrification. During all the study, chemical species were quantified by ionic chromatography (IC25, 2003, DIONEX, USA). Ammonium, VSS, COD were determined using standard methods. The reactor was operated over a 120 days period in sequencing batch mode with a cycle composed of alternating aerobic period (nitrification) and anoxic period (denitrification), followed by settling (20 minutes) and withdraw (8 minutes). Aerobic period was initiated by the feeding of ammonium-rich effluent ($20 \text{ mL}\cdot\text{min}^{-1}$, 10 min) and anoxic period started with addition of complementary solution respectively ($6.25 \text{ mL}\cdot\text{min}^{-1}$, 2.5 to 7.5 minutes). During the first 35 days of operation (case A), nitrification and denitrification durations were fixed to 100 minutes and 180 minutes respectively. Then automatic control of aerobic and anoxic durations has been activated based on DO and ORP signals with the method described below (cases B, C, D).

Calculations

The N_2O gas phase concentration measured is converted into emission rate (ER) with the following equation, considering that N_2O behave like an ideal gas. The total amount of N_2O emitted during an aerated period is calculated by integration of the N_2O -ER. Emissions factor (noted EF) is calculated as the ratio of N_2O emission to the amount of ammonium removed.

$$\text{N}_2\text{O-ER} (\text{gN-N}_2\text{O}\cdot\text{L}^{-1}\cdot\text{h}^{-1}) = \text{N}_2\text{O}(\text{ppmv}) \cdot 10^{-6} \cdot Q_{\text{gas}}(\text{L}\cdot\text{h}^{-1}) \cdot V\text{m}^{-1} (25.0376 \text{ L}\cdot\text{mol}^{-1} \text{ at } 28.0 \text{ }^\circ\text{C} \text{ and } 1 \text{ atm}) \cdot 2 \cdot M_{\text{N}} (14.00674 \text{ g}\cdot\text{mol}^{-1}) \cdot V^{-1} (\text{L liquid medium})$$

The concentration of free nitrous acid (HNO_2 , noted FNA) is calculated according to (Anthonisen et al., 1976).

Results and discussion

Example of a typical SBR cycle

A typical cycle of the SBR obtained after 45 days of operation (phase B) is presented in Figure 1 (a). Ammonium is fed during the first 10 minutes (period 1) of the aerobic period with a volumetric exchange ratio of 12.3 %. In that example, it corresponds to a total amount of ammonium to nitrify of $56.7 \text{ mgN-NH}_4^+\cdot\text{L}^{-1}$ which is partly oxidized into nitrite during this feeding period as nitrification takes place as soon as period 1 begins. Aeration is maintained (period 2) until the depletion of ammonium. All the nitrified ammonium was converted into nitrite as nitrite oxidation was stopped after 40 days due to the operational conditions. Actually, Nitrite Oxidising Bacteria (NOB) were outcompeted due to simultaneous effect of ammonium inhibition, substrate privation (aeration is stopped after ammonia depletion) and high temperature (growth rate of ammonium oxidizing bacteria becoming higher than those of NOB). Aeration is interrupted from periods 3 to 6 maintaining anoxic condition. Period 3 corresponds to the introduction of 18.75 ml of secondary solution (organic carbon source) into

the reactor. Then, nitrite was removed by denitrification (periods 3 and 4). After the exhaustion of nitrite, a settling period (period 5) was followed by a last decanting period (period 6). Emission of N_2O is observed throughout the aerobic period. The N_2O profile in the gas phase shows a maximum (28.9 ppm). After that, the rate of N_2O emission decreases according to the decrease of nitrification rate. In this example, 1.84% (emission factor) of the amount of nitrogen oxidized during the aerobic period has been transformed into N_2O . During all the study, N_2O was mainly emitted during aerobic periods. Emissions during the anoxic phase were quantified punctually by using nitrogen gas injection and were negligible compared to aerobic emissions, which can be explained by a sufficient COD/N ratio during denitrification period. It was also observed that the anoxic N_2O production was limited if the aeration was stopped after the end of N_2O peak emissions, i.e. a few minutes after the ammonium depletion.

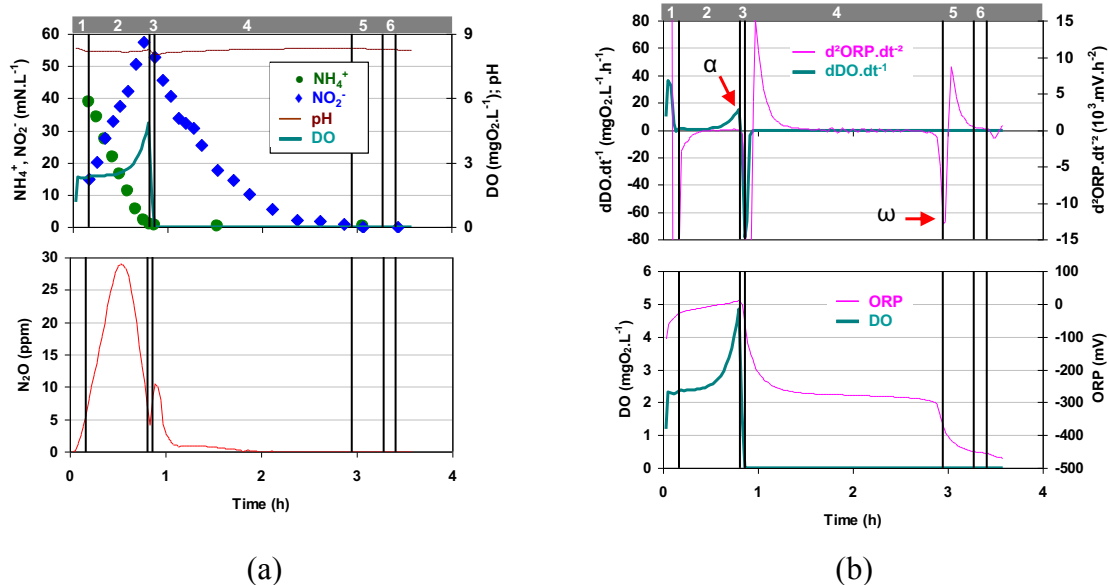


Figure 1. (a) Evolution of $N-NH_4^+$, $N-NO_2^-$, DO, pH and N_2O during nitrification and denitrification. (b) Evolution of DO, ORP, the first derivative of DO and the second derivative of ORP during nitrification and denitrification.

Automatic control system

Evolution of DO, ORP, the first derivative of DO and the second derivative of ORP are presented in Figure 1 (b). DO increases rapidly as soon as the cycle begins, then stabilizes during nitrification period and starts to increase again when ammonia is depleted. The point α is determined by a threshold limit on DO derivative, corresponding to the end of nitrification. In the meanwhile ORP decreases during anoxic period and this rate accelerates as soon as the nitrite is depleted (commonly attributed to the start of sulfate reduction activity). The point ω corresponding to the end of denitrification is detected with a threshold limit on the second derivative of ORP. The automatic control system is based on these signals. When the point α is reached, this signifies that ammonium is depleted and the system automatically moves to the next period of the cycle. Similarly, the end of denitrification is detected when the point ω is reached and the system moves automatically to the settling period. Threshold values used for the control of the cycle presented in Figure 1 (b) are $14 mgO_2.L^{-1}.h^{-1}$ and $-12000 mV.h^{-2}$ for α and ω respectively. The first and second derivatives are calculated with linear regression associated to the 15 last data which correspond to the last 5 minutes. The use of derivatives signals allows the system to be relatively insensitive to possible drift of DO and ORP absolute values due to calibration default.

Effect of the control strategy on performances and N₂O emissions

The impact of automatic control, cycle configuration and operating parameters has been analyzed on 4 successive case studies presented in Table 1. Period A corresponds to the reference condition with constant duration of aerobic and anoxic periods. The control system has been activated during case studies B, C and D. In addition, cycle configuration was slightly adapted during phases C and D (configuration 2): an aerated period (15 minutes) before the feeding of ammonium-rich wastewater has been introduced and the aerated period has been extended by 20 to 40 additional minutes after the exhaustion of ammonium (α). A step-feed mode was tested during phase C, and different air flow rates and COD/N ratios were also compared. For each case study, a same operating condition was maintained during at least 10 cycles.

Table 1. Characteristics of four successive case studies (with subcase) of the operating SBR.

Case study	Automatic control	Cycle configuration	Step-feed	NH ₄ ⁺ removed (mgN.L ⁻¹)	COD/N	Qgas (L.h ⁻¹)
A	NO	1	1	55.0	4.5	70
B1	YES	1	1	55.0	4.5	111.4
B2					3.4	
C1	YES	2	5	68.7	4.1	54.8
C2					6.5	26.1
D1	YES	2	1	51.0	5.0	111.4
D2				36.0	8.4	83.1
D3						

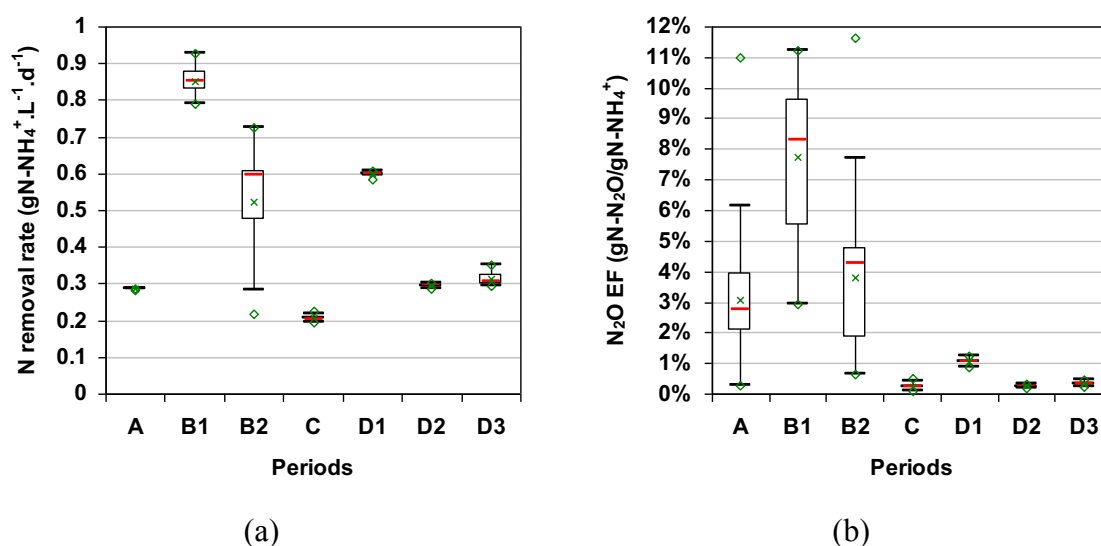


Figure 2. Statistic distributions of the evolution of the nitrogen removal rate (a) and N₂O emission factor (b) during four different case studies. The median is represented with red thick lines, the average with green crosses, extreme values with green triangles, whiskers with vertical black lines delimited with horizontal black lines on top and bottom.

After 40 days of operation (5 days after the transition to case B), the shunt of nitrate has been established and it was maintained until the end of the study. Evolution of nitrogen removal performances and N₂O emissions during the four case studies are represented with boxplot in Figure 2 a and b respectively. Compared to the reference phase (case A), the automatic control without optimization of the configuration of cycles (B1, B2) improves the nitrogen

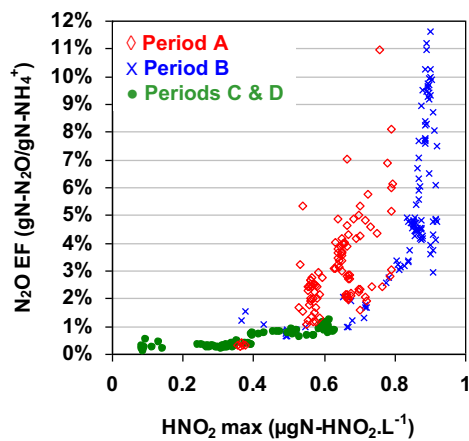
removal performance of the process (increasing the median of nitrogen removal rate from 0.29 $\text{gN-NH}_4^+ \cdot \text{L}^{-1} \cdot \text{d}^{-1}$ for case A to 0.85 $\text{gN-NH}_4^+ \cdot \text{L}^{-1} \cdot \text{d}^{-1}$ and 0.60 $\text{gN-NH}_4^+ \cdot \text{L}^{-1} \cdot \text{d}^{-1}$ for subcases B1 and B2 respectively) but dramatically impacts the N_2O emission factor, increasing the median of this factor between cases A, B1 and B2 (2.74 % for case A, 8.30 % and 4.28 % for subcases B1 and B2 respectively). A high variability of the N_2O emission factor is observed both for the reference period (case A) with time based system (configuration 1) and with the automatic control without modification of the cycle configuration (B1, B2). The transition between configuration 1 and configuration 2 (additional short initial aerobic phase, introduction of a time delay after the end of nitrification) allows reducing N_2O emissions while controlling nitrogen removal performances. A mean N_2O -EF of 1.0 % is obtained for a mean nitrogen removal rate of 0.60 $\text{gN-NH}_4^+ \cdot \text{L}^{-1} \cdot \text{d}^{-1}$ for the subcase D1. These values are managed by the amount of ammonium removed for periods automatically controlled by the system coupled to the optimized configuration. For subcases D2 and D3, this pair of mean values decreases to [0.27 % - 0.30 $\text{gN-NH}_4^+ \cdot \text{L}^{-1} \cdot \text{d}^{-1}$] and [0.32 % - 0.31 $\text{gN-NH}_4^+ \cdot \text{L}^{-1} \cdot \text{d}^{-1}$] respectively. The feeding of ammonium in 5 steps (case C) allows decreasing the mean N_2O -EF to 0.24 % with a mean nitrogen removal rate of 0.21 $\text{gN-NH}_4^+ \cdot \text{L}^{-1} \cdot \text{d}^{-1}$.

Relation between FNA concentration and N_2O emission factor

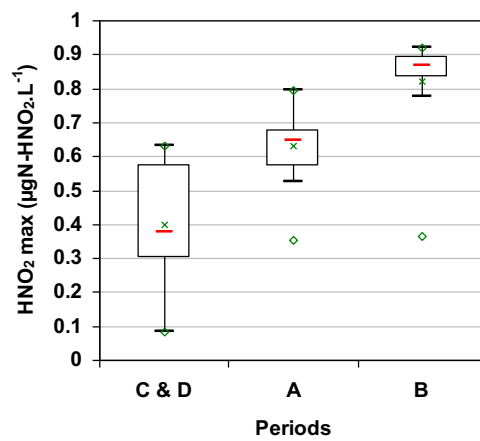
For each cycle the maximal nitrite and free nitrous acid concentrations (reached at the end of aerobic phase) were measured or calculated. On one hand, a large variation of N_2O emissions was observed for the same level of nitrite concentration and no clear relationship can be demonstrated between these parameters (not shown here). On the other hand, the relationship between the maximum free nitrous acid concentration and N_2O emission factor appears clearly in Figure 3 a. It appears that the N_2O emission factor is exponentially correlated to the free nitrous acid concentration with a threshold value around 0.70 $\mu\text{gN-HNO}_2 \cdot \text{L}^{-1}$ beyond which the N_2O emission factor increases significantly with a great dispersion. This observation is close to those presented in (Lemaire et al., 2011). Indeed, these authors have found that an FNA concentration lower than 0.80 $\mu\text{gN-HNO}_2 \cdot \text{L}^{-1}$ leads to an N_2O -EF lower than 1.0 %. The range of FNA concentration corresponding to each case is presented in Figure 3 b with a statistic distribution illustrated by box plots. The largest dispersion of N_2O emission factors (case B) has been obtained for the smallest dispersion of FNA concentrations. This can be explained by the fact that another parameter (see below DO effect) influences the emissions during this period. On the contrary, in cases C and D, low values of N_2O -EF and relatively small dispersion of N_2O -EF corresponds to a large dispersion of FNA concentrations whose maximum value is located below the threshold value.

Relation between DO concentration and N_2O emission factor

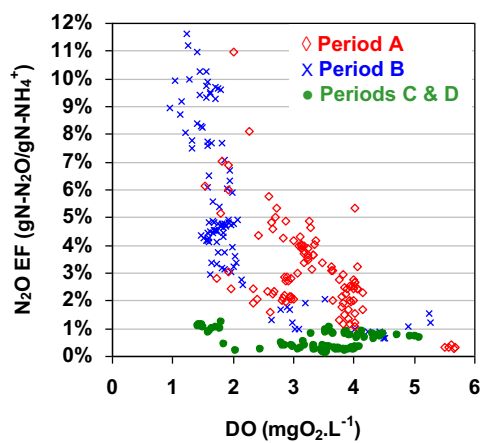
The N_2O emission factor versus DO is presented in Figure 3 c (average value of DO throughout the aerobic period). The statistic distribution of oxygen concentrations in cases A, B, C and D is presented Figure 3 d. For cases A and B, emissions of N_2O increases when DO decreases. Highest emission factors (3 to 12% of nitrogen removed) were observed at low DO in case B, which is simultaneously the case with highest concentration of FNA. In cases C and D, the effect of DO does not appear clearly; N_2O emission factors remain lower than 1.22 % throughout these periods despite an important variability of the dissolved oxygen concentration from 1.42 $\text{mgO}_2 \cdot \text{L}^{-1}$ to 5.10 $\text{mgO}_2 \cdot \text{L}^{-1}$. In different previous studies higher emission of N_2O was detected at low DO concentrations (Kampschreur et al., 2009; Pijuan et al., 2014). But in this study, this effect is more pronounced for cycles operated with the cycle's configuration 1 (cases A and B) than those operated with the configuration 2 (case C and D).



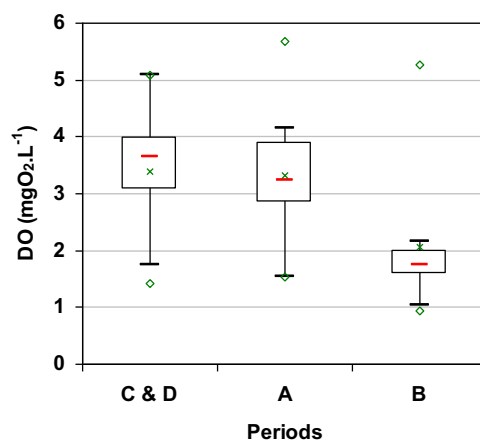
(a)



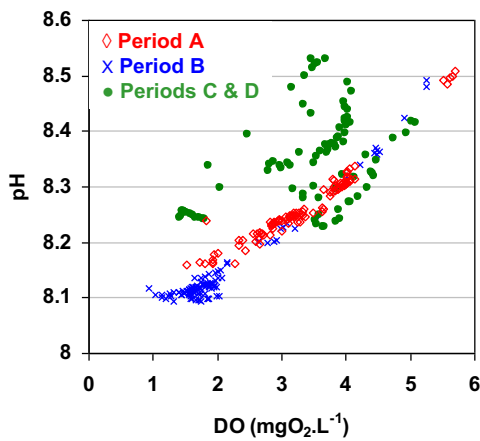
(b)



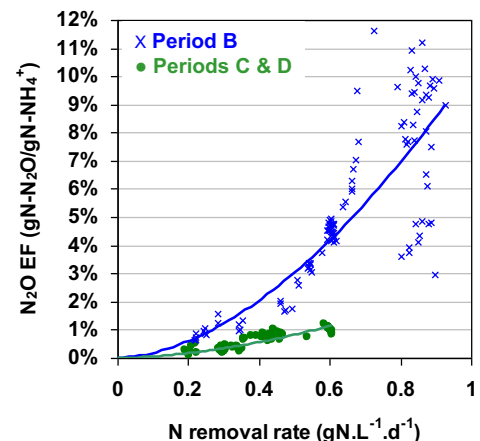
(c)



(d)



(e)



(f)

Figure 3. Maximum free nitrous acid concentration (a) and average DO during nitrification (c) *versus* N₂O EF for case studies A, B, C and D. Statistic distributions of the free nitrous acid concentration (b) and DO (d) during case studies. Average pH during nitrification *versus* DO (e) during case studies. N₂O EF *versus* nitrogen removal rate for case studies B, C and D (constant nitrogen removal rate with a high N₂O EF variation during phase A). Lines correspond to trend curves relative to the different data series. Each point corresponds to a SBR cycle. For statistic distributions, the median is represented with red thick lines, the average with green crosses, extreme values with green triangles, whiskers with vertical black lines delimited with horizontal black lines on top and bottom.

Correlated effects of operational parameters

A correlation (almost linear) appears between DO and pH for cases A and B. Variation of DO and pH depends mainly on two similar factors: (1) the variation of biodegradable COD present in aerobic phase which controls the CO₂ production by heterotrophic activity and influences the DO for a given air flow rate and (2) the variation of air flow rate which controls the stripping rate of CO₂ and the DO as well. In this study the presence of biodegradable COD during nitrification in aerobic phase is due to residual organic matter not used during the previous anoxic phase for cycles operated with the configuration 1. This excess leads both to DO and pH decrease, the later leading to an increase of FNA as this concentration is directly correlated to the pH value. For cases C and D, the correlation between DO and pH does not appear. Indeed, the introduction of the aerobic period before ammonium feeding allows removing the residual organic matter and increasing the pH with the stripping of inorganic carbon. The extension of the aerated period after the depletion of ammonium also allows increasing the pH as well. Thus, the optimization of the configuration leads to the decorrelation between DO and pH during nitrification and for a given DO concentration, the pH will be higher with the configuration 2 leading to a lower free nitrous acid concentration. This can partly explain the relation between DO and N₂O-EF in Figure 3 c. Below a pH value of 8.2, the FNA concentration crosses the threshold value of 0.70 µgN-HNO₂.L⁻¹ for cases A and B corresponding to a DO lower than 2.5 mgO₂.L⁻¹ (Figure 3 e). For cases C and D, the pH is higher for this range of DO and FNA concentrations remain lower than 0.70 µgN-HNO₂.L⁻¹.

Control strategies for the mitigation of N₂O emissions in SBR

Results clearly demonstrated the benefit of the control system based on configuration 2 (periods C, D) for minimising N₂O emission factor. The N₂O emission factor as a function of the nitrogen removal rate is presented in Figure 3 f. Highest emissions of N₂O were clearly observed for case B, with a low DO, high FNA concentration and high nitrogen removal rates. For a given nitrogen removal rate and a given DO concentration the N₂O-EF is lower with the optimized configuration (C and D). Thus, this optimized control system allows exploring interesting ranges of DO and nitrogen removal rates in term of process performances while, at the same time, limits the accumulation of FNA concentration, thus reducing significantly emissions of N₂O.

Finally several recommendations can be proposed for N₂O emission mitigation in SBR with nitrification / denitrification over nitrite:

- (1) Limit the presence of readily biodegradable COD during nitrification which impacts the competition between nitrifiers and heterotrophs on oxygen, decreases the DO and possibly the pH during nitrification. This was done in this study by introducing an aerobic phase before N-rich effluent feeding, this could be done also by an optimal pre-anoxic (DN) phase in SBR systems receiving wastewater containing both COD and ammonium.
- (2) Limit the accumulation of FNA below 0.70 µgN-HNO₂.L⁻¹. This can be done by limiting the amount of ammonium to be removed during nitrification (step-feed, reduction of the volumetric exchange ratio) or by increasing the pH. It was done in this study by means of a 5-step feed strategy (case C) coupled to a slight increase of the pH due to modification of cycle configuration.
- (3) Extend the aerobic period after the exhaustion of ammonium. The system avoids switching in anoxic conditions as the N₂O emitted by AOB during nitrification is not finished (extension of the aerobic period after the detection of the DO bending point).

Conclusions

An automatic control system for nitrification / denitrification over nitrite is presented in this study. The DO and ORP bending points allow detecting the end of nitrification and denitrification respectively. By adapting the length of aerobic and anoxic periods, the system allows to outcompete NOB and maintain full conversion of ammonia into nitrite.

Several effects on N₂O emissions were highlighted during nitrification. (1) The N₂O-EF is exponentially correlated to the free nitrous acid concentration with a threshold value of 0.70 µgN-HNO₂.L⁻¹ beyond which the N₂O-EF increases significantly.

(2) The effect of DO on N₂O EF is exacerbated for cycles with a high FNA accumulation.

(3) The presence of easily biodegradable COD during nitrification increased the N₂O-EF.

The optimisation of control system allows reducing the N₂O emission factor to less than 1% for a nitrogen removal rate of 0.6 gN-NH₄⁺.L⁻¹.d⁻¹. Moreover, N₂O emission factor could be limited to less than 0.2% for a nitrogen removal rate of 0.3 gN-NH₄⁺.L⁻¹.d⁻¹.

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