

Partial nitrification of high ammonia concentration wastewater as a part of a shortcut biological nitrogen removal process

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Abstract

Biological nitrification–denitrification is the most common process for nitrogen removal from wastewaters. During the first step, ammonia is aerobically oxidized to nitrite and then to nitrate. Subsequently, this nitrate is reduced to gaseous nitrogen by denitrifying microorganisms that use it as final electron acceptor. Shortcut biological nitrogen removal is based on the fact that nitrite is an intermediary compound in both steps: a partial nitrification up to nitrite is performed followed by nitrite denitrification. This will produce savings in aeration during the nitrification step. This research studies the effect of dissolved oxygen concentration in nitrite accumulation. An activated sludge reactor is operated under different DO levels, analyzing nitrite accumulation and ammonia removal. Results show that at 1.4 mg DO/L, 75% of nitrite accumulation takes place, with 95% of ammonia removal. Moreover, nitrite accumulation showed to be stable over more than 170 days of operation. Under these conditions, a reduction of 40% in the value of the required mass transfer coefficient K_La is achieved.

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1. Introduction

Biological nitrogen removal through nitrification–denitrification is based on natural nitrogen cycle transformations. As with any other biological treatment system, it uses the same tools as nature to transform pollutants. The difference is that these processes take place inside reactors, where favourable conditions are used to speed up transformation reactions. Nitrification–denitrification process takes place in two steps. The first one, nitrification, consists of the aerobic oxidation of reduced nitrogen compounds (ammonia and nitrite) by the action of autotrophic microorganisms, which obtain their energy from these reactions. Nitrification involves two steps: ammonia oxidation to nitrite and the subsequent nitrite oxidation to nitrate. Different microorganisms are responsible for each step [1]. Fig. 1 shows ammonia and nitrite conversion reactions during nitrification.

The second step, denitrification, is an anoxic process performed by heterotrophic microorganisms that use nitrite and nitrate as final electron acceptors. Organic matter (electron donor) is therefore required during denitrification.

Operational costs of the biological nitrogen removal process are to a great extent related to the oxygen and organic matter requirements for nitrification and denitrification, respectively. Some new processes and operational strategies have arisen during the last few years in order to reduce these costs. One of these is the shortcut to biological nitrogen removal. This process is based on the fact that nitrite is an intermediary compound in both steps: nitrification and denitrification. Therefore, it will be convenient to produce a partial nitrification up to nitrite and then denitrification starting from this nitrite (Fig. 2). This approach will produce savings in the oxygen needs during nitrification, a reduction in the denitrification organic matter requirements, plus a decrease in surplus sludge production.

Partial nitrification requires the reduction of the activity of nitrite oxidizing bacteria, without affecting ammonia oxidizing microorganisms. Variation of the aeration level

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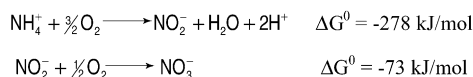


Fig. 1. Ammonia conversion reactions during nitrification.

seems to be an interesting possibility to achieve this, since oxygen affinity constants of ammonia and nitrite oxidizers are different: 0.3 and 1.1 mg/L, respectively [1]. Therefore, operation at low dissolved oxygen concentration should reduce the activity of nitrite oxidizing bacteria to a greater extent, producing nitrite accumulation [2–7].

On the other hand, shortcut biological nitrogen removal requires denitrification starting from nitrite, which is indeed toxic at high concentrations. Several researches have shown that denitrifying sludge can be acclimated to nitrite, considered an adaptation process [8,9].

The present research studies the feasibility of a partial nitrification process, using a low dissolved oxygen concentration in order to reduce the activity of nitrite oxidizers, and maximize nitrite accumulation.

2. Materials and methods

2.1. Activated sludge reactor set-up

A 2.9 L useful volume-activated sludge reactor was used to conduct this study; the settler volume was 1.5 L. The reactor was operated at a pH of 7.8, which was automatically controlled by the addition of 80 g/L bicarbonate solution. The reactor temperature was kept at 25 °C through an immersion electrical heater connected to a temperature control device. The dissolved oxygen concentration was controlled by adjusting airflow rate. During the operation at low aeration levels, a mechanical stirrer was used in order to ensure good mixing and suspension of solids. Fig. 3 shows a schematic representation of the nitrifying activated sludge reactor. Seed sludge was obtained from a laboratory nitrification reactor already in operation for several months. The reactor was fed with a synthetic wastewater produced by dilution of concentrated media adapted from Campos et al. [10]. The composition of the concentrated wastewater is shown in Table 1.

2.2. Analytical methods

Nitrate was determined by UV absorption at 220 and 275 nm and nitrite by the sulphanilamide acid reaction [11].

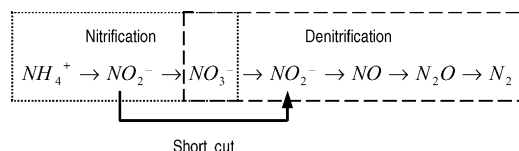


Fig. 2. Nitrification–denitrification with nitrite accumulation.

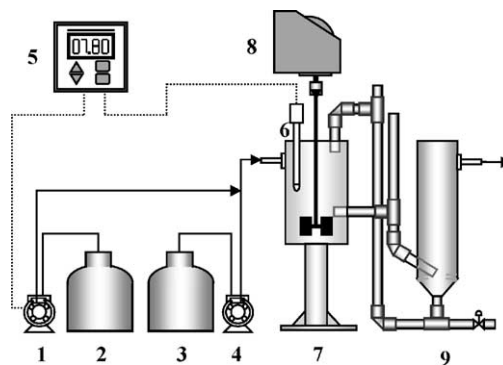


Fig. 3. Schematic diagram of the experimental set-up of the nitrifying activated sludge reactor: (1) pH control pump, (2) bicarbonate solution tank, (3) feed tank, (4) feed pump, (5) pH controller, (6) pH sensor, (7) oxidation tank, (8) stirrer, (9) settler.

Ammonia was determined using an ion selective electrode (Orion 95-12). Solids were measured by gravimetric method [11]. Dissolved oxygen was determined using a portable oxygen electrode (WTW OXI 323). In order to determine biomass activity, respirometric tests were performed, using sludge samples taken from the reactor. Tests were carried out as described by Campos [12], using a 200 mL BOD bottle, equipped with an oxygen sensor (Orion 97-08) connected to a data logger device. The bottle was filled with phosphate buffer (1.43 g/L KH_2PO_4 and 7.47 g/L K_2HPO_4) and aerated to oxygen saturation. Then, substrate and previously washed sludge were added. Biomass and initial substrate concentration were 1 g VSS/L and 15 mg N/L, respectively. Oxygen consumption was continuously monitored until total depletion. Respirometric activity was calculated as the maximum oxygen consumption rate. Ammonia and nitrite were used as substrates in different assays in order to discriminate the activity of ammonia and nitrite oxidizing bacteria.

2.3. Reactor operation

Activated sludge operation was divided in three steps: start-up, operation at different dissolved oxygen concentra-

Table 1
Concentrated synthetic wastewater composition

Concentrated synthetic wastewater		Traces nutrient solution	
Compound	Concentration (mg/L)	Compound	Concentration (mg/L)
NH_4Cl	19120	$\text{EDTAH}_2\text{Na}_2 \times 2\text{H}_2\text{O}$	50000
MgSO_4	625	$\text{ZnSO}_4 \times 7\text{H}_2\text{O}$	2200
KH_2PO_4	2500	CaCl_2	5540
$(\text{NH}_4)_2\text{SO}_4$	23560	$\text{MnCl}_2 \times 4\text{H}_2\text{O}$	5060
NaCl	20000	$\text{FeSO}_4 \times 7\text{H}_2\text{O}$	5000
Traces solution	5 (mL/L)	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \times 4\text{H}_2\text{O}$	1100
		$\text{CuSO}_4 \times 5\text{H}_2\text{O}$	1570
		$\text{CoSO}_4 \times 7\text{H}_2\text{O}$	1900
		KOH	To pH 6

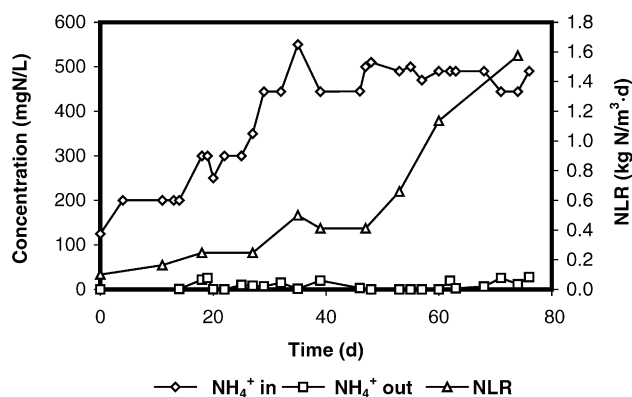


Fig. 4. Ammonia concentration (inlet and outlet) and NLR during start-up of the nitrifying activated sludge reactor.

tions, and further operation at the selected DO level. During start-up, nitrogen loading rate (NLR) was increased from 0.1 to 1.5 kg N/m³ d, through the increment of ammonia concentration and reduction of hydraulic retention time. Once a NLR of 1.5 kg N/m³ d was achieved, it was fixed for the rest of the reactor operation. Hydraulic retention times for the reactor and the whole system (reactor plus settler) were 7 and 10.5 h, respectively. DO concentration was reduced in four steps: 2.4, 1.4, 1 and 0.5 mg/L. Each condition was maintained for at least 7 days. Ammonia removal and nitrite accumulation were determined for each condition. Finally, the activated sludge reactor was operated for 170 days at the DO concentration that produced the higher nitrite accumulation without affecting ammonia removal, in order to study the long-term stability of partial nitrification.

3. Results and discussion

Fig. 4 presents the applied nitrogen loading rate, with the inlet and outlet ammonia concentrations, during the start-up of the activated sludge reactor. NLR was increased from 0.1 to 1.5 kg N/m³ d, raising the ammonia concentration and

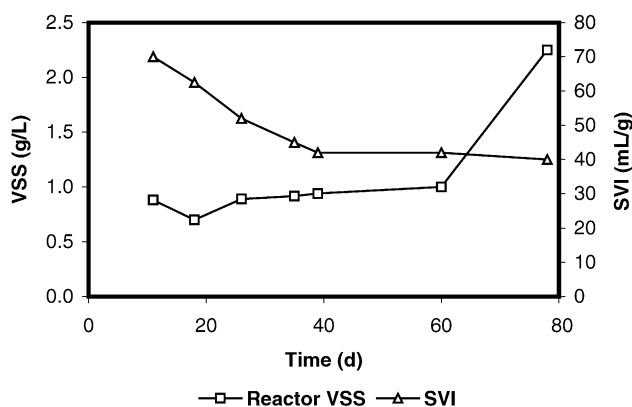


Fig. 5. Mixed liquor volatile suspended solids and sludge volumetric index during start-up of the nitrifying activated sludge reactor.

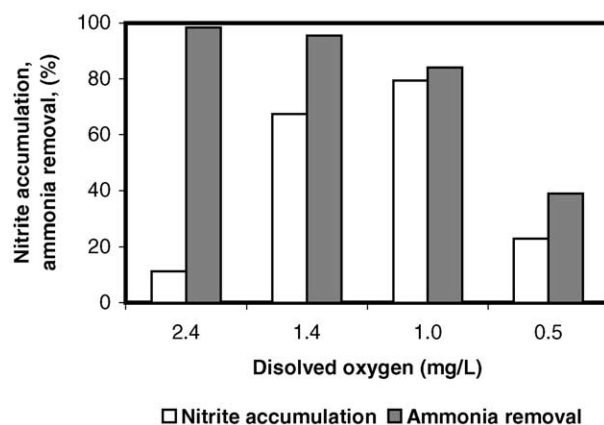


Fig. 6. Nitrite accumulation and ammonia removal during the operation of activated sludge nitrifying reactor at different dissolved oxygen concentrations.

reducing the hydraulic retention time. Ammonia influent final concentration was 500 mg N/L. Ammonia effluent concentration never exceeded 20 mg N/L, which represents over 95% nitrogen removal. Dissolved oxygen was kept over 4 mg/L during start-up; therefore, no nitrite was detected during this period. Fig. 5 presents the evolution of biomass concentration (measured as volatile suspended solids) and volumetric sludge index (SVI) during start-up procedure. Once biomass concentration reached 2.5 g VSS/L, purges were performed in order to maintain that concentration. SVI experienced a slight decrease, getting close to 40 mL/g, showing sludge excellent settling properties.

Once the start-up procedure was finished, the dissolved oxygen concentration was changed in order to determine its effect on nitrite accumulation. Results are summarized in Fig. 6. Nitrite maximum accumulation happened at a DO level of 1.0 mg/L. Nevertheless, at that concentration ammonia removal was affected. Therefore, a dissolved oxygen concentration of 1.4 mg/L was selected in order to operate the activated sludge reactor, since it promotes a high level of nitrite accumulation, preserving a high ammonia removal.

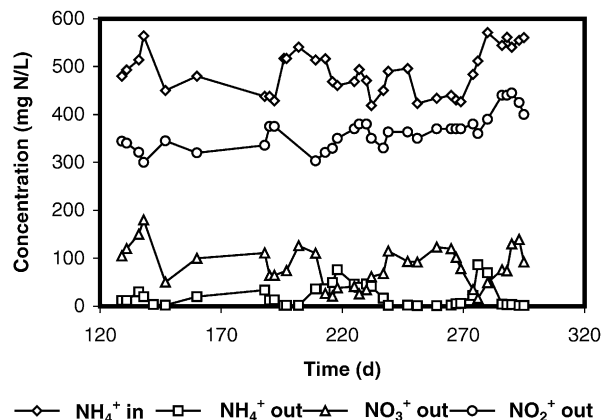


Fig. 7. Ammonia (inlet and outlet), nitrite (outlet) and nitrate (outlet) concentrations during the operation of the nitrifying activated sludge reactor at 1.4 mg DO/L.

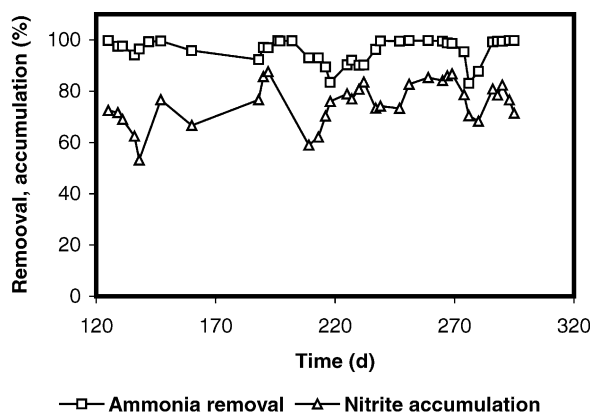


Fig. 8. Ammonia removal and nitrite accumulation during the operation of the nitrifying activated sludge reactor at 1.4 mg DO/L.

Under similar conditions, Ruiz et al. [7] found an optimum DO concentration in the range 0.7–1.5 mg/L. This difference is probably due to the high floc densities attained in this research, which produces higher oxygen mass transfer limitations.

Fig. 7 presents the operation of the reactor at 1.4 mg DO/L. Ammonia outlet concentrations remained low during the whole period. Only around days 220 and 275, it increased to over 30 mg N/L, due to problems with the aeration system. Nitrite remained in the range of 300–400 mg N/L.

Fig. 8 presents ammonia removal and nitrite accumulation during the activated sludge operation at 1.4 mg DO/L. Ammonia conversion was over 90% during the operation time, with the exception of days around 210 and 275 already mentioned. Nitrite accumulation was close to 75%. This shows that the activity of nitrite oxidizing bacteria had been successfully reduced, and no adaptation had taken place. Therefore, the control of oxygen concentration is a useful tool to achieve a stable partial nitrification.

Fig. 9 presents the maximum oxygen uptake registered during respirometric tests performed to determine biomass activity. Assays performed with nitrite as substrate measure the activity of the bacteria that use this compound as source

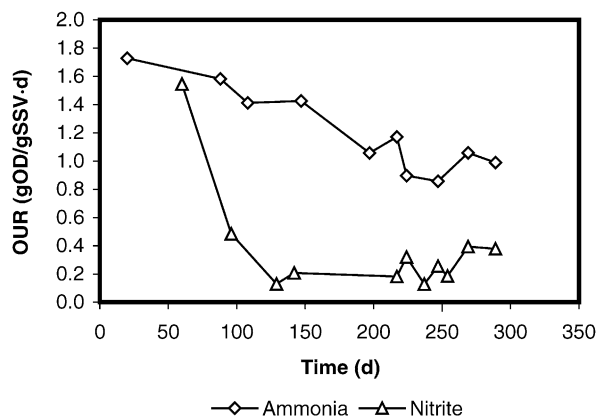


Fig. 9. Maximum oxygen uptake rate (OUR) during respirometric assays from sludge from activated sludge nitrifying reactor, measured with ammonia and nitrite as substrate.

of energy. If ammonia is used as substrate, then the activity of both groups influence the response, since under normal conditions, the nitrite produced is also consumed. The respirometric activity of nitrite oxidizing bacteria reduced notoriously once start-up finished and reduction of the DO concentration in the reactor started (day 80). This confirms that the operation at low oxygen concentrations was an effective way to reduce the activity of these microorganisms. It is not clear if this reduction is the result of a decrease in microorganism specific activity or biomass washout. Ammonia respirometric activity also experienced a decrease, but to a much lower extent (close to 35%). The initial reduction can be attributed at some level to the decrease of nitrite oxidizers activity. From day 130, the activity of nitrite consumers remains constant, but ammonia respirometric activity continued reducing. Therefore, some detriment in the activity of ammonia consumers also occurred. Anyway, this reduction did not affect the performance of the reactor. Under reactor conditions, oxygen consumption calculated with substrate removal and considering the nitrite accumulation was around 0.8 kg DO/m³ d, which was lower than the maximum oxygen uptake given by respirometry. More research in the effect of low oxygen concentration of both bacterial groups is needed in order to clarify this point.

One of the main advantages of partial nitrification is the reduction of energy requirements associated with aeration. This is achieved by decreasing the oxygen requirement, up to 25% for complete nitrite accumulation. For the nitrite accumulation level obtained in this study (around 75%), the oxygen requirement reduction is 19%. Moreover, if oxygen concentration is used to produce the nitrite accumulation, as was the case of this research, there is a further reduction in aeration requirement due to the increase in the oxygen mass transfer rate. Since the reactor operates at the minimum feasible oxygen concentration, the difference between DO concentration and equilibrium concentration ($C - C^*$) is higher in comparison with a full nitrification process. The oxygen transfer rate is a function of the oxygen concentration and the global volumetric mass transfer coefficient $K_L a$.

$$N = K_L a (C^* - C) \quad (1)$$

where N is the oxygen transfer rate (which must be equal to the oxygen requirements of the nitrification process), $K_L a$ is the volumetric global mass transfer coefficient, C^* is the equilibrium oxygen concentration and C represents the actual oxygen concentration. In the case of a partial nitrification process, Eq. (1) transforms to

$$N_P = K_{LP} (C^* - C_P) \quad (2)$$

where the subscript P refers to a partial nitrification process.

Combining both equations:

$$\frac{K_{LP}}{K_{La}} = \frac{N_P (C^* - C)}{N (C^* - C_P)} \quad (3)$$

Eq. (3) represents the reduction in the required $K_L a$ due to a partial nitrification operation strategy. The reduction in

oxygen requirement is 19%, so $N_P = 0.81$ N at a DO of 1.4 mg/L. The DO concentration required for complete nitrification is close to 3.5 mg/L. Replacing these values in Eq. (3) yields a 40% reduction in the required mass transfer coefficient, which will certainly have a positive impact on operational costs.

4. Conclusions

The shortcut nitrification–denitrification operation strategy for nitrogen removal offers several advantages over the traditional process. Aeration requirements during the nitrification step can be noticeably reduced. Partial nitrification can be achieved by reducing the oxygen concentration in the nitrifying reactor. By this means, nitrite oxidizing bacterial activity can be selectively reduced. After 170 days of operation, ammonia oxidizers seemed to be also affected, but to an extent that did not affect ammonia removal during the activated sludge operation. A high level of nitrite accumulation can be obtained in long-term operation (several months) with a nitrifying activated sludge at 1.4 mg DO/L. Under the conditions of this study, a reduction of 40% in the value of the required mass transfer coefficient K_{La} was achieved, which certainly represents an important reduction in treatment costs.

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