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Nitrification with high nitrite accumulation for the treatment of wastewater with high ammonia concentration

G. Ruiz[a], D. Jeison[b], R. Chamy[a,*]

[a] Biochemical Engineering School, Universidad Católica de Valparaíso, General Cruz 34, Valparaíso, Chile
[b] Department of Chemical Engineering, Universidad de La Frontera, Casilla 54-D, Temuco, Chile

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Abstract

The objective of this paper was to determine the best conditions for partial nitrification with nitrite accumulation of simulated industrial wastewater with high ammonia concentration, lowering the total oxygen needed in the nitrification step, which may mean great saving in aeration. Dissolved oxygen (DO) concentration and pH were selected as operational parameters to study the possibility of nitrite accumulation not affecting overall ammonia removal. A 2.5 L activated sludge reactor was operated in nitrification mode, feeding a synthetic wastewater simulating an industrial wastewater with high ammonia concentration. During the start-up a pH of 7.85 and a DO of 5.5 mg/L were used. The reactor was operated until stable operation was achieved at final nitrogen loading rate (NLR) of 3.3 kg N– NH_4^+/m^3 d with an influent ammonia concentration of 610 mg N–NH_4^+/L.

The influence of pH was studied in continuous operation in the range of 6.15–9.05, changing the reactor pH in steps until ammonia accumulation (complete nitrification inhibition) took place. The influence of DO was studied in the same mode, changing the DO in steps from 5.5 to 0.5 mg/L.

The pH was not a useful operational parameter in order to accumulate nitrite, because in the range of pH 6.45–8.95 complete nitrification to nitrate occurs. At pH lower than 6.45 and higher than 8.95 complete inhibition of nitrification takes place. Setting DO concentration in the reactor at 0.7 mg/L, it was possible to accumulate more than 65% of the loaded ammonia nitrogen as nitrite with a 98% ammonia conversion. Below 0.5 mg/L of DO ammonia was accumulated and over a DO of 1.7 mg/L complete nitrification to nitrate was achieved.

In conclusion, it is possible under the conditions of this study, to treat high ammonia synthetic wastewater achieving an accumulation of at least 65% of the loaded nitrogen as nitrite, operating at a DO around 0.7 mg/L. This represents a reduction close to 20% in the oxygen necessary, and therefore a considerable saving in aeration.

Keywords: Nitrification; Nitrite accumulation; Activated sludge; Dissolved oxygen; pH

1. Introduction

Biological nitrification-denitrification is the most commonly used process for nitrogen removal from wastewater, especially for municipal wastewater. Research has been done in the application of this process to industrial wastewater with high ammonia concentration [1–5]. Due to the high oxygen demand for ammonia oxidation, aeration is the main cost in this system.

Nitrification is carried out in two steps. First ammonia is converted to nitrite by ammonia oxidizing bacteria. In the second step nitrite oxidizing bacteria convert nitrite to nitrate as shown in Fig. 1. For 1 mol of ammonia, ammonia oxidizing bacteria use 1.5 mol of oxygen and nitrite oxidizing bacteria 0.5 mol of oxygen. Complete nitrification requires 2 mol of oxygen per mol

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*Corresponding author. Tel.: +56-32-273641; fax: +56-32-273803.

E-mail address: rchamy@ucv.cl (R. Chamy).

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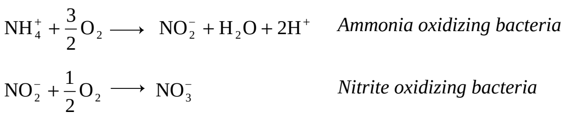
of nitrogen to be nitrified. This means that partial nitrification to nitrite will only require 1.5 mol of oxygen per mol of nitrogen, implying a 25% less oxygen demand for partial nitrification compared to complete nitrification.

In the denitrification process nitrate is converted to nitrite and then to nitrous oxide and nitric oxide and finally to nitrogen gas, each step consuming COD. If postdenitrification is considered, partial nitrification to nitrite, i.e., a shortcut of the nitrate would mean a reduction in the total COD required for denitrification, because no COD is needed for the conversion of nitrate to nitrite [5].

For these reasons partial nitrification to nitrite may be attractive because it may result in a reduction in the oxygen demand in the nitrification step which means a saving in aeration and afterward a reduction in the COD required for postdenitrification.

Some work has been done to achieve partial nitrification to nitrite [6–8], but in these cases low influent ammonia concentrations were used. There have been no studies with high ammonia concentration, simulating industrial wastewater, where the main problem would be the high nitrite concentration, which may produce inhibition of the nitrification biomass.

To achieve partial nitrification it is necessary to reduce the activity of nitrite oxidizing bacteria but not the activity of ammonia oxidizing bacteria. This would be done by assuring favourable conditions for ammonia oxidizing bacteria development. Table 1 presents the kinetic expressions usually accepted for nitrifying biomass [9]. It can be seen that substrate concentration, temperature, pH and DO affect each activity in different terms, because the value of each constant is different. Additionally pH will affect the substrate concentration for each step, because of the modification of the acid–base equilibrium.



$$NH_4^+ + \frac{3}{2}O_2 \longrightarrow NO_2^- + H_2O + 2H^+ \quad \textit{Ammonia oxidizing bacteria}$$

$$NO_2^- + \frac{1}{2}O_2 \longrightarrow NO_3^- \quad \textit{Nitrite oxidizing bacteria}$$

Fig. 1. Ammonia conversions in nitrification.

Within these variables, substrate concentration is not an operational parameter because it is the objective variable in terms of wastewater treatment. Temperature will affect the growth rate of both types of bacteria in different ways: ammonia oxidizers should have superior growth rates at high temperatures than nitrite oxidizers. This is indeed the idea behind the SHARON process. However in most cases the temperature is not susceptible to be modified and controlled in full-scale reactors, mainly for economic considerations. So pH and DO concentration may be the main manipulated variables to control the system.

The objective of this paper was to study the influence of pH and DO concentration on nitrite accumulation in the nitrification process, and in this way, to achieve a considerable saving in aeration. Moreover, this process strategy may mean an additional saving in the amount of COD to be added in the denitrification step.

2. Material and methods

2.1. Experimental set-up

An activated sludge unit consisting of a reaction tank of 2.5 L of useful volume and an external settler was used (Fig. 2). The aeration was controlled by adjusting the air flow level to the desired oxygen concentration. The pH was automatically controlled by adding a

Table 1
Kinetic expressions for ammonia oxidizing and nitrite oxidizing bacteria [9][a]

Bacterial group	Kinetic expression
Ammonia oxidizing bacteria	$\mu = \mu_{\max} \dfrac{\lvert NH_4^+\rvert}{K_{SH}\cdot e^{(A_E/T)}10^{-pH} + \lvert NH_4^+\rvert + \dfrac{\lvert NH_4^+\rvert^2}{K_{IH} e^{\cdot(A_E/T)}\, 10^{-pH}}} \dfrac{\lvert O_2\rvert}{K_{O2} + \lvert O_2\rvert}$
Nitrite oxidizing bacteria	$\mu = \mu_{\max} \dfrac{\lvert NO_2^-\rvert}{K_{SH}\cdot e^{(A_E/T)}\cdot 10^{-pH} + \lvert NO_2^-\rvert + \dfrac{\lvert NO_2^-\rvert^2}{K_{IH}\cdot e^{(A_E/T)}\cdot 10^{-pH}}} \dfrac{\lvert O_2\rvert}{K_{O2} + \lvert O_2\rvert}$

[a] Kinetics coefficients are also temperature dependent which may be found elsewhere [9]. This relationships are not considered here for simplicity. μ: Specific growth rate; $\mu_{\max}$: maximal specific growth rate; K_{SH}: saturation coefficient for the unionised substrate; K_{IH}: inhibition coefficient for the unionised substrate; K_{O2}: oxygen saturation coefficient; $\lvert NH_4^+\rvert$: ammonia concentration; $\lvert NO_2^-\rvert$: nitrite concentration; $\lvert O_2\rvert$: dissolved oxygen concentration; $e^{(A_E/T)}$: equilibrium constant for the dissociation of the substrates, where A_E is the activation energy and T the absolute temperature.

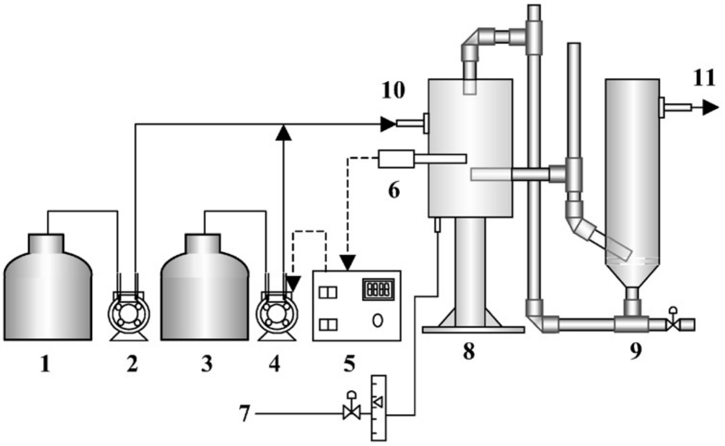


Fig. 2. Schematic diagram of the experimental set-up of the activated sludge unit: (1) feed tank, (2) feed pump, (3) bicarbonate tank, (4) bicarbonate pump, (5) pH controller, (6) pHmeter, (7) air line, (8) reactor, (9) settler, (10) reactor inlet and (11) reactor outlet.

solution of 80 g/L of $NaHCO_3$, used as pH buffer and carbon source for nitrifying bacteria. Temperature was maintained at 30°C. The reactor was seeded with sludge coming from a nitrifying activated sludge reactor already in operation for more than 1 year.

For the start-up the reactor was operated for 175 d until stable operation was achieved. Because the hydraulic residence time was 5.7 h, stable operation was assumed once the response of the system was maintained for 2 days (4.2 hydraulic retention times). Synthetic wastewater was used with an ammonia nitrogen concentration of 610 mg $N–NH_4^+$/L and a nitrogen loading rate (NLR) of 3.3 kg $N–NH_4^+/m^3$ d. The feed was prepared by diluting the concentrated synthetic wastewater with tap water to the desired concentration. The composition of the concentrated synthetic wastewater (10 g$N–NH_4^+$/L), adapted from [10], is presented in Table 2. During the start-up operation, the pH and DO concentration were kept constant at 7.85 and 5.5 mg/L, respectively.

After day 70 a stable operation was achieved, without significant changes in the removal rates. After start-up, the pH and DO concentration were changed in steps, as indicated in Table 3.

In the first study, the pH was changed in steps from 7.85 to 6.35 (acid range), allowing enough time to achieve a stable operation at each pH condition. After this study, the reactor was operated for 10 d at pH 7.85 in order to reactivate the biomass. Finally, the pH was changed in steps from 7.85 to 9.05 (basic range).

After the study of the influence of the pH, the reactor was operated to reactivate the biomass. In the second study, the DO concentration was changed in steps from 5.5 to 0.5 mg/L, achieving a stable operation for each condition.

Table 2
Concentrated synthetic wastewater (10 g$N–NH_4^+$/L) and trace nutrient solution composition

Compound	Concentration (mg/L)
Concentrated synthetic wastewater	
NH_4Cl	19120
$MgSO_4$	625
H_2PO_4	2500
$(NH_4)_2SO_4$	23560
NaCl	20000
Trace solution	5 (mL/L)
Trace nutrient solution	
$EDTAH_2Na_2 \cdot 2H_2O$	50000
$ZnSO_4 \cdot 7H_2O$	2200
$CaCl_2$	5540
$MnCl_2 \cdot 4H_2O$	5060
$FeSO_4 \cdot 7H_2O$	5000
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1100
$CuSO_4 \cdot 5H_2O$	1570
$CoSO_4 \cdot 7H_2O$	1900
KOH	to pH 6

2.2. Analytical methods

Ammonia was analyzed using an ion selective electrode (Orion 95-12). Nitrate was determined by UV absorption at 220 and 275 nm and nitrite by the Sulfanilamide acid reaction [11]. DO concentration was measured with an oxygen electrode (YSI-95, YSI Company). Ammonia, nitrite, nitrate were determined daily, oxygen concentration twice a day and biomass (as VSS) every 3 d.

Table 3
pH and DO values during the experiments

	pH study (constant DO = 5.5 mg/L)		DO Study (constant pH = 7.85)
Days	Study at pH lower than 7.85	Days	DO (mg/L)
0–24	7.85	0–2	5.5
25–60	7.15	3–6	4.7
61–110	6.85	7–17	3.7
111–116	6.15	1--20	2.7
117–170	6.85[a]	21–27	1.7
171–186	6.55	28–31	1.4
187–191	6.35	32–44	0.7
192–194	6.55[a]	45–49	0.5
195–220	6.45		
	Study at pH over 7.85		
221–230	7.85		
231–268	8.35		
269–289	8.65		
290–303	8.95		
304–313	9.05		

[a] The pH was changed to the previous value due to inhibition of the system.

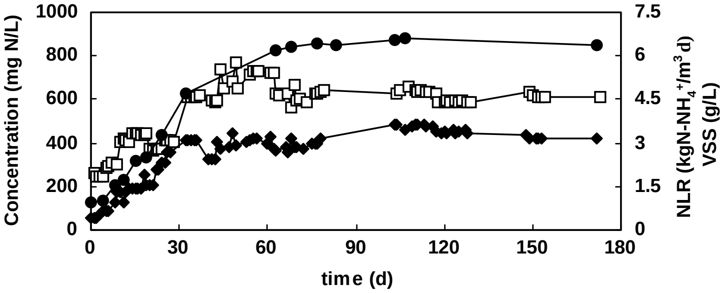


Fig. 3. Start-up of the nitrification unit. (□) NH4 in (mg N–NH$_4^+$/L), (●) VSS (gVSS/L), (♦) (NLR kg N–NH$_4^+$/m^3 d).

3. Results and discussion

3.1. start-up

As seen in Fig. 3, nitrogen loading rate (NLR) was incremented from 0.5 to 3.3 kg N–NH$_4^+$/m^3 d, changing both the ammonia concentration in the influent from 260 to 610 mg N–NH$_4^+$/L and the feed flow from 3.8 to 10.6 L/d. The pH was automatically controlled between 7.8 and 7.9.

A biomass concentration of 6.3 gVSS/L was maintained throughout the experiment with a continuous mixed liquor purge (started on day 50). As can be seen in Fig. 3 from day 70 the NLR and ammonia concentration were kept constant and stable operation was considered. Complete nitrification was achieved over the start-up period (Fig. 4).

3.2. pH influence

Fig. 5 presents the results obtained for the pH effect experiments. In the acid range (below 7.85), from 7.85 to pH 6.45 there was no effect on nitrification, but at pH lower than 6.35 complete inhibition of nitrification took place. After the study in the acid range, the reactor was operated at pH 7.85 in order to reactivate the biomass. After this reactivation period, the study of the influence of the pH on nitrite accumulation in the basic range of pH was started. No influence of pH was observed between pH 7.85 and 8.95 (see Fig. 5), even if temporal nitrite accumulation took place at pH 8.65 and 8.95. At pH 9.05, complete inhibition of nitrification took place with no nitrite accumulation.

These results show that complete nitrification took place in a wide range of pH studied (between pH 6.45

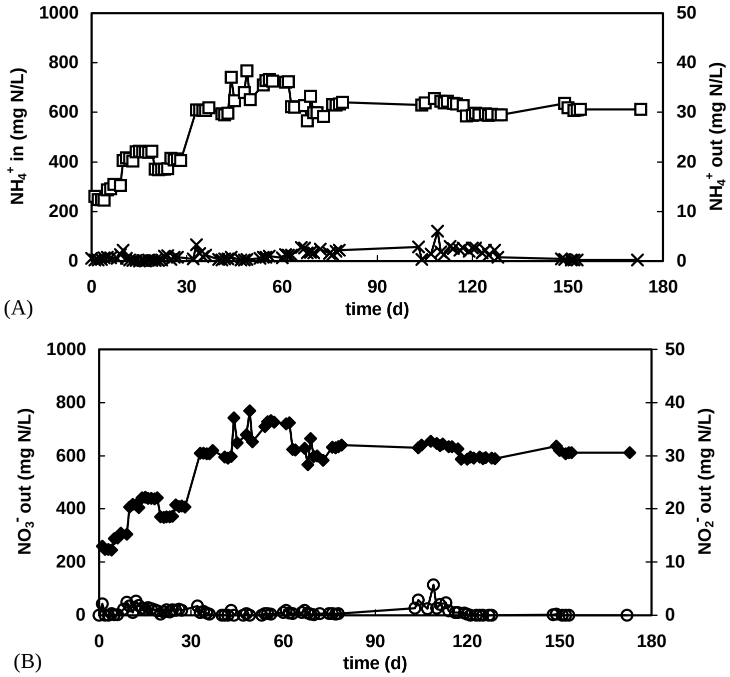


Fig. 4. Variation of NH_4^+ (A) and NO_3^- and NO_2^- (B) during the start-up of the system. (□)mg NH_4^+ in (mg N–NO_4^-/L), (X)NH_4^+ out (mg N– NH_4^+/L), (o) NO_2^- out (mg N–NO_2^-/L), (♦) NO_3^- out (mg N–NO_3^-/L).

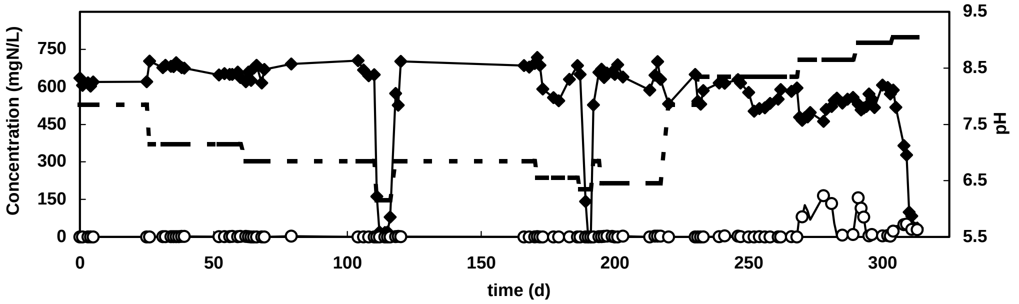


Fig. 5. Time course of the study of the influence of pH (dotted line) on nitrite accumulation. $[NH_4^+]_{feed}$ 610 mg N–NH_4^+/L, [DO] 5.5 mg/L. (o) NO_2^- out (mg N–NO_2^-/L), (♦) NO_3^- out (mg N–NO_3^-/L).

and 8.95). At pH lower than 6.45 and over 8.95 complete inhibition of nitrification with no nitrite accumulation was observed. Fig. 6 summarizes the results of the study of pH on nitrite accumulation.

The behaviour for the pH effect was expected for basic pH, due to free ammonia inhibition to both ammonia and nitrite oxidizing bacteria, reported previously [12]. The same authors explain that at acid pH only nitrite oxidizing bacteria are inhibited by free nitrous acid. But in this study both groups of bacteria were inhibited. This may mean that free nitrous acid may produce an inhibition of ammonia oxidizing bacteria which was not previously reported.

Suthersan and Ganczarcczyk [13] found that nitrite accumulation was achieved at high pH, suggesting that it is possible to accumulate nitrite controlling the pH. In our work, temporal nitrite accumulation took place especially after a change in the pH set value, but due to biomass adaptation, complete nitrification was achieved in a few days (see Fig. 5). Continuous culture and enough time for adaptation may explain why no nitrite accumulation was achieved at the end of each pH value

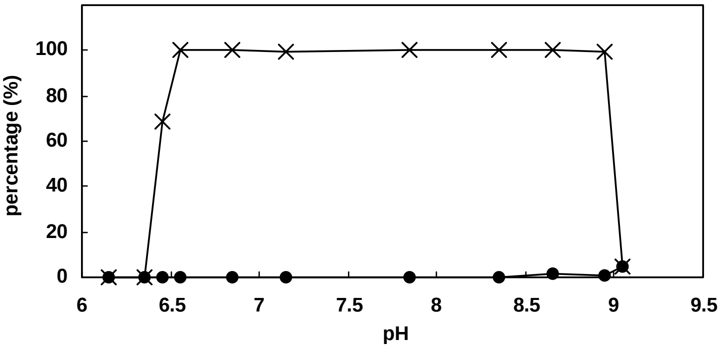


Fig. 6. Influence of pH on the percentage of ammonia oxidized and nitrite accumulation. (X) percentage of ammonia consumption, (●) percentage of nitrite accumulation.

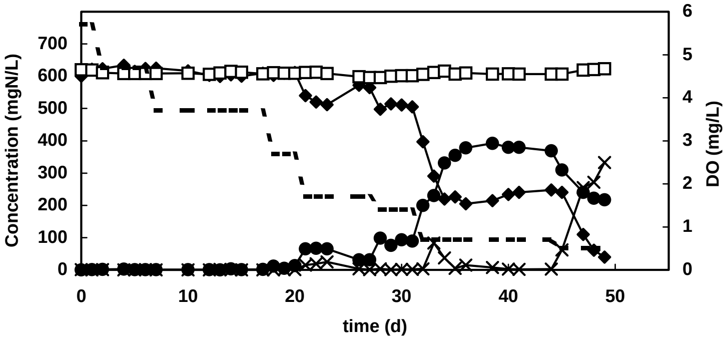


Fig. 7. Time course of the study of the influence of DO concentration (dotted line) on nitrite accumulation. $[NH_4^+]_{feed}$ 610 mgN–NH_4^+/L, pH 7.85 mg/L. (☐) NH_4^+ in (mg N–NH_4^+/L), (X) NH_4^+ out (mg N–NH_4^+/L), (●) NO_2^- out (mg N–NO_2^-/L), (◆) NO_3^- out (mg N–NO_3^-/L).

experiment. This means that it is not possible to accumulate nitrite on a long term basis using pH as a key parameter.

3.3. DO influence

Fig. 7 presents the behaviour of the system during consecutive changes in DO values. It can be seen that DO has no influence on nitrite accumulation at values of 5.7–2.7 mg/L. At a DO of 1.7 mg/L there was a temporal accumulation of nitrite and at a DO of 1.4 and 0.7 mg/L accumulation increased with the same ammonia consumption. At a DO of 0.5 mg/L, both nitrite accumulation and ammonia consumption decreased.

Fig. 8 summarises these results. Each point is the mean of the stable operation for each condition. It can be seen that nitrite accumulation starts at a DO of 1.7 mg/L with a maximum at 0.7 mg/L, with complete ammonia consumption.

These results show that under the conditions of this study it is possible to operate the system on a long term basis, i.e., for 12 d (more than 50 hydraulic retention times) at DO of 0.7, with at least 65% of the NLR accumulated as nitrite with 98% of ammonia conversion. Based on stoichiometry this accumulation implies a 17% reduction in the oxygen needed for nitrification (1.67 mol of oxygen per mol of ammonia nitrogen compared to 2 for complete nitrification) which will mean a saving in aeration. As was stated before, the accumulation of nitrite will mean a further saving in the COD needed for postdenitrification.

4. Conclusion

Over a wide range of pH it is possible to achieve complete nitrification (between pH 6.45 and 8.95). At pH lower than 6.45 and above 8.95 nitrification suddenly fell and complete inhibition of both ammonia oxidizing and nitrite oxidizing bacteria took place.

Nitrification was not affected by DO from 5.7 to 1.7 mg/L, but at a DO of 1.4 mg/L nitrite accumulation

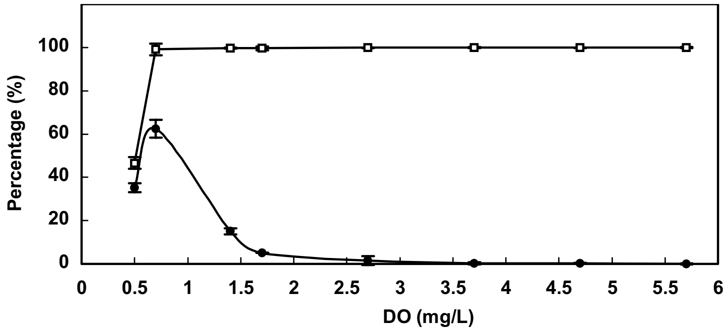


Fig. 8. Influence of DO concentration on the percentage of ammonia oxidised and nitrite accumulation. (□) percentage of ammonia consumption, (●) percentage of nitrite accumulation. Each point is the mean of the stable operation in each condition. Bars indicate three standard deviations of the data.

took place and increased while the DO concentration decreased but did not affect the overall ammonia conversion. Maximum nitrite accumulation, within the values of DO studied, occurred at a DO concentration of 0.7 mg/L. At a DO of 0.5 mg/L ammonia conversion is affected which means that ammonia accumulation takes place.

Under the conditions of this study, it is possible to accumulate at least 65% of the NLR as nitrite with 98% of ammonia conversion on a long term basis (for 12 d at a DO of 0.7 mg/L). Based on stoichiometry this means around a 17% reduction in the oxygen needed for nitrification. This reduction will produce a saving in aeration and the accumulation of nitrite will mean a further saving in the COD needed for postdenitrification.

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