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Effects of Aeration Rates and Patterns on Shortcut Nitrification and Denitrification

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Abstract

The effects of aeration rates and aeration patterns on the oxidation of ammonia-nitrogen into nitrite were investigated. The influent high ammonia-nitrogen synthetic wastewater resembled to those of the catalytic process of the petrochemical refinery. The method involved the biological shortcut nitrification and denitrification lab-scale's sequencing batch reactor (SBR) process based on intermittent aerations and aeration patterns. All the operations were carried out in a 20 L working volume SBR bioreactor, and the influent synthetic wastewater's concentration was always 1000 mg/L ammonia-nitrogen NH_4-N concentration at a C/N (carbon/nitrogen) ratio of 2.5:1. Effective shortcut nitrification to nitrite was registered at 1.1 mg-O_2/L (*i.e.* 9 L-air/min) with 99.1% nitrification efficiency, 99.0% nitritation rate and 2.6 mg- NO_3^--N/L nitrate concentration. The best results with 99.3% nitrification efficiency were recorded when operating at 1.4 mg-O_2/L (*i.e.* 12 L-air/min). According to these experiments, it results that the nitrite accumulation rate was related to aeration rate and cycle's duration. However, at 1.7 mg-O_2/L (*i.e.* 15 L-air/min), the system was limited by an increase in nitrate concentration with more than 5 mg/L which could be a point of reverse to conventional nitrification. The best total nitrogen (TN) removal was about 71.5%.

Keywords

Wastewater Treatment, SBR, Partial Nitrification/Denitrification, Intermittent Aeration, Aeration Rate, Aeration Pattern, Total Nitrogen (TN) Removal

1. Introduction

Uncontrolled ammonia-nitrogen (NH_4^+-N) discharge into natural water reservoirs

(lake, river, pond, etc.) has resulted in eutrophication phenomenon and dissolved oxygen (DO) depletion along with the extinction of aquatic bio-communities [1] [2]. Regulation of ammonia-nitrogen discharge into natural water resources by limiting the effluent ammonia-nitrogen standard between 5 and 15 mgN/L depending to countries led up to a rapid development of various technologies.

Conventionally ammonia-nitrogen removal was realized by methods of physical chemistry [3] [4] and/or biological processes [5]. Among these technologies, biological nitrogen removal (BNR) was found to be less expensive, environmentally safe, and thus sound. Conventional BNR consists of autotrophic nitrification with NH_4^+-N oxidized to nitrate (NO_3^-) via nitrite (NO_2^-) under high aeration condition (about 4.57 g O_2/g NH_4^+-N), and the subsequent heterotrophic denitrification of nitrate to nitrogen gas by the addition of external carbon source [6] [7] (2.86 g COD/g NO_3^--N) as following equations:

1) Nitrification phase:

a) $NH_4^+ + 2HCO_3^- + 1.5O_2 \rightarrow NO_2^- + 3H_2O + 2CO_2$

("Nitritation" by Ammonia oxidizing bacteria AOB)

b) $NO_2^- + 0.5O_2 \rightarrow NO_3^-$

("Nitratation" by Nitrite oxidizing bacteria NOB)

2) Denitrification phase:

$$NO_3^- + 1.08CH_3OH + H^+ \rightarrow 0.47N_2 + 0.76CO_2 + 2.44H_2O + 0.065C_5H_7O_2N$$

(by denitrifiers or heterotrophs).

However, the requirement of high aeration during autotrophic nitrification [8] along with the supply of external carbon source during the subsequent heterotrophic denitrification [6] [7] increased the process's overall costs. Therefore, limiting the aeration amount for the nitrification without retarding ammonia-nitrogen oxidation and reducing the external carbon supply during the denitrification become new challenges for engineers and researchers. Thus, in order to address these issues, the recent development of partial nitrification/denitrification process has seen to be an alternative technique to replace the conventional nitrification since it led to 25% aeration savings along with the elimination or a 40% reduction of external carbon supply [9] [10] [11] [12] [13]. In fact, partial nitrification and denitrification process involves the restriction of nitrification phase to only nitrite (NO_2^-) production (nitritation) followed by direct nitrite reduction to nitrogen gas (N_2) during denitrification phase (denitritation) thus inhibiting nitrate (NO_3^-) production phase (nitratation) as showed below:

a) Partial nitrification or nitritation

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

b) Denitritation

$$2NO_2^- + 6H^+ + 6e^- \rightarrow N_2 + 2OH^- + 2H_2O$$

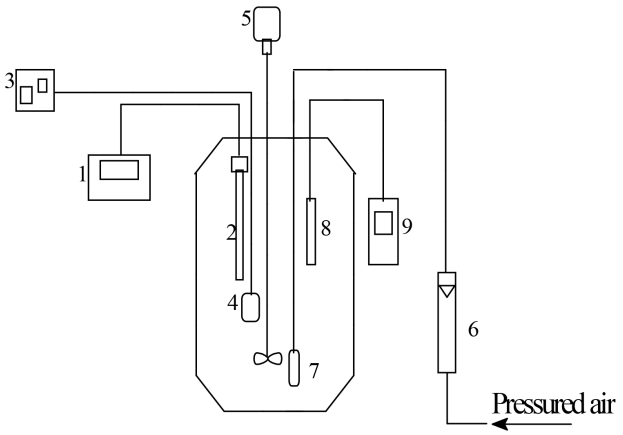
The success of partial nitrification/denitrification process relies on the control of factors such as temperature, pH, DO [14] [15]. Several models using this process have been recently developed [16] [17].

Sequencing batch reactor (SBR) is one of the most popular biological technique used to remove nutrient contaminants specially ammonia-nitrogen from several kind of wastewater [17]-[26]. It has the ability to operate by cycle, and this latter may consist of four or five steps comprising fill, react, settle and draw/idle. Moreover, another advantage of SBR is that all process can be performed in only one tank and therefore the costs of the construction and the operational requirements are alleviated [16] [17] [18]. On the other hand, SBR partial nitrification process operating with intermittent A/O aeration pattern has a benefit when treating alkalinity deficient high ammonia-nitrogen wastewater since part of the alkalinity consumed during aerobic phase was recovered during the next anoxic phase thus reducing the external alkalinity and the carbon sources addition [26]. Several authors have reported nitrogen removal from municipal and industrial ammonia-rich wastewaters by means of various SBR partial nitrification and denitrification processes [17] [20] [21]-[26].

The purpose of this study was to investigate, the effects of different aeration rates on the ammonia-nitrogen removal via nitrite method when treating a high ammonium-nitrogen wastewater (1000 mg NH_4^+-N/L influent concentration) by mean of 16 hrs cycle's SBR process; and on the other hand, to compare the possible effects of two series of two types of aeration patterns on total nitrogen (TN) removal when treating the above synthetic wastewater simulating the one from catalytic process of the petrochemical refinery.

2. Materials and Methods

2.1. Experimental Apparatus



1. pH-meter; 2. pH sensor; 3. Temperature controller; 4. heater 5. Stirrer; 6. Air rotameter; 7. Air stone diffuser; 8. DO-sensor; 9. DO-meter.

Figure 1. Experimental lab-scale SBR.

2.2. Characteristics of Influent Wastewater

The influent synthetic wastewater, simulating the one from catalytic process of the petrochemical refinery, was essentially composed by ammonium bicarbonate (NH_4HCO_3) and glucose ($C_6H_{12}O_6{\cdot}7H_2O$) which served as main nitrogen and

carbon source, respectively. The C/N ratio was established to 2.5:1. Table 1 below shows the complete composition of the wastewater.

The ammonium bicarbonate was chosen as nitrogen source because it dissolves easily and affords a certain amount of alkalinity (as $CaCO_3$) which alleviates the continuous addition of external alkaline solution.

2.3. Analytical Methods

NH_4^+-N concentration was determined following the methods described in the "Water Quality-Determination of Ammonium-Distillation and titration method" [27]. The analysis of NO_2^--N and NO_3^--N were realized by ion chromatography (Dionex ICS-1000 system, USA). Mixed liquor suspend solids (MLSS) and mixed liquor volatile suspend solids (VSS) were determined using Whatman GF/A filters in accordance with the methods developed in the standard methods for the examination of water and wastewater [28]. DO and pH were measured by LDO-meter (Hach Portable HQ40d LDO meter USA) and pH-meter (pH-meter Delta 320, Mettler Toledo Instrument Ltd, USA), respectively. Aeration was provided by electric air pump (Air pump ACO-002, Xingjiang SanLin, Ltd, China) and the airflow rate was diffused through stone diffusers placed at the bottom of the reactor and the airflow rate was regulated by air rotameter (LZB-4WBF rotameter, Jiangsu Tianyuan Instrument Co., Ltd., China) in order to obtain the desired DO level.

2.4. Activated Sludge Acclimation

The activated sludge was that one used in previous study on shortcut-nitrification and denitrification operations which characteristics have changed due to continuous feeding operations without wasting. In the present operations, its average MLSS and MLVSS concentrations were maintained at 7 ± 0.5 gSS/L and 6.1 ± 0.5 gVSS/L with a VSS/SS ratio of 0.83 and SVI of 130.

2.5. Operational Methods

All the operations were carried out inside the 20 L working volume SBR (Figure 1)

Table 1. Synthetic wastewater characteristics.

Parameters	Values (mg/L)
$C_6H_{12}O_6{\cdot}7H_2O$(glucose)	2500
NH_4HCO_3 (ammonium bicarbonate)	1000
M (KH_2PO_4)	100
Mg^{2+} ($MgSO_4$)	50
Fe^{2+} ($FeSO_4{\cdot}7H_2O$)	4
Ca^{2+} ($CaCl_2$)	15
Mn^{2+} ($MnSO_4{\cdot}H_2O$)	15
K^+ (KCl)	35

with 10 L of the above 1000 mg NH_4-N /L concentration influent synthetic wastewater (Table 1) and 10 L of the acclimated activated sludge. The exchange volume ratio was set to 50% resulting in a real 500 mg/L NH_4-N concentration inside the SBR. Each SBR cycle consisted of five steps which were fill, react, settle, draw and idle. The influent was filled by pulse addition without aeration allowing the removal of part of the remaining nitrite and nitrate coming from previous cycles. An overhead stirrer provided continuous mixing and the temperature was controlled at 25˚C ± 2˚C while the pH adjusted to 7.5 - 8.5 by means of HCl or Na_2CO_3 solution as the case. MLSS and MLVSS were maintained, by means of sludge wasting before settle phase, at 7 ± 0.5 g SS/L and 6.1 ± 0.5 g VSS/L, respectively.

The first experiment is to examine the feasibility of shortcut nitrification and denitrification under this above conditions. It consists of operating the reactor with 10 L influent containing 1000 mg/L NH_4-N concentration and 10 L of activated sludge under a fixed 9 L-air/min aeration rate (average 1.1 mg-O_2/L) with a 16 h cycle composed of 16 sub-cycles with each 1h sub-cycle consisting of alternating 45 min aerobic phase and 15 min anoxic phase (each 1 h sub-cycle equals 45/15 min AAA phases).

The following operations are conducted in order to compare the effects on ammonia-nitrogen removal via nitrite accumulation when working at aeration rates of 3, 6, 9, 12 and 15 L-air/min, corresponding to average DO concentrations of 0.2, 0.8, 1.1, 1.4 and 1.7 mg-O_2/L, respectively.

Thereafter, a 16h cycle's operation is conducted at fixed 9 L-air/min aeration rate (average 1.1 mg-O_2/L) with aeration pattern including another sub-cycle of 15 min aerobic phase and 45 min anoxic phase (15/45-min AAA phases). The aim of this operation is to compare the total nitrogen (TN) removal efficiency with the one obtaining during the above sub-cycle of 45/15-min AAA phases.

At the end, similar comparison is performed between operations of 16 h cycle involving sub-cycles of 50/40 AAA phases and 40/50-min AAA phases at the same aeration rate of 9 L-air/min (average 1.1 mg-O_2/L) condition.

3. Results and Discussion

3.1. Study of Shortcut Nitrification and Denitrification at Different Aeration Rate

Figures 2(a)-(c) below shows the cycle's profiles of nitrogen species (NH_4-N, NO_2-N and NO_3-N), DO concentration and pH during operations at 9 L-air/min aeration rate (average 1.1 mg-O_2/L) with each sub-cycle composed by 45/15min AAA phases. The ammonia-nitrogen loading rate was 0.74 kgNH_4-N/m^3. d. Complete NH_4-N oxidation lasted 16 h (Figure 2(a)). Both nitrification efficiency and nitritation rate were nearly 99% and the nitrate concentration was less than 3.9 mg/L (Table 2) which is in accordance with a shortcut nitrification and denitrification process. The rapid nitrification observed during these operations is probably due to long aerobic phase over short anoxic period. It can be seen on

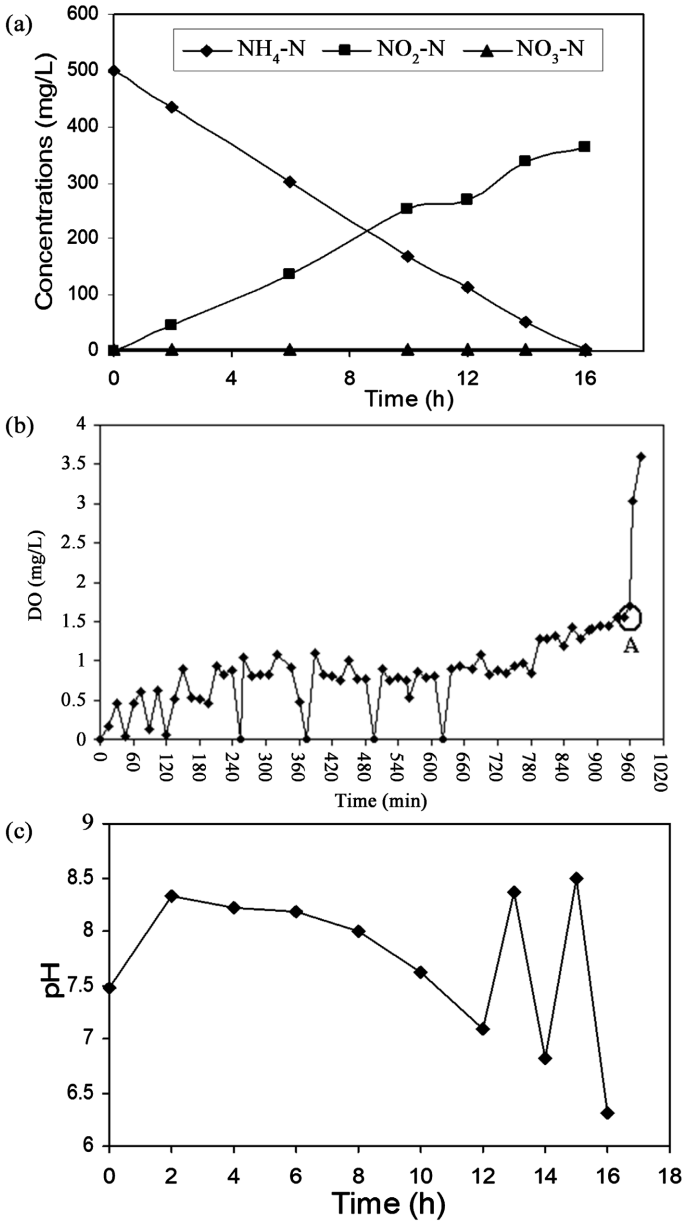


Figure 2. Cycle (with sub-cycles of 45/15min AAA) profiles of NH_4-N, NO_2-N and NO_3-N (a); DO (b); and pH (c).

Table 2. TN removals under sub-cycles of 45/15 and 15/45min.

Parameters	Alternate aeration patterns	
	45/15min	15/45min
$[NH_4\text{-}N]_{effluent}$ (mg /L)	4.5	3.2
$[NO_3\text{-}N]_{effluent}$ (mg /L)	3.9	2.3
$[NO_2\text{-}N]_{effluent}$ (mg/L)	3.6×10^2	2.0×10^2
Nitrification efficiency (%)	98.9	99.3
Nitritation rate (%)	98.6	98.9
TN removal rate (%)	25.9	58.6

Figure 2(b) that the DO concentration is very low at the beginning of operation (120 min) giving an average DO concentration of 0.3 mg-O_2/L. This is in accordance with the low nitrification period observed at the beginning of the cycle related to high activities of denitrifying organisms which limited the substrate accessibility to ammonia-oxidizing bacteria (AOB). After that, the recorded DO concentration is increasing to nearly 1.0 mg-O_2//L for most of the aeration phase therefore speeding the nitrification process. However, it can be seen (Figure 2(b)) that some recorded DO values are sometimes under the detection limits. This is probably related to the applied aeration pattern which consists of alternating aeration and anoxic phases. From 780 min (13 h), a slight increase of DO concentration is observed and continues to increase reaching nearly 1.5 mg/L at 960 min (16 h) showing the ammonia breakpoint in point A (Figure 2(b)) marking the end of the nitrification phase or in other words the complete oxidation of ammonia-nitrogen to nitrite. From this A point, the DO concentration was increased drastically to quickly reach about 3.5 mg/L confirming the end of nitrification via nitrite route.

Figure 2(c) shows the evolution of pH profiles during these operations. At the beginning of operations, it clearly indicates the pH increase from 7.5 to 8.3 during the first 2 h due to the high carbon dioxide (CO_2) produced early by the denitrification phase. Thereafter, the pH decreased slightly to about 8.0 and then quickly dropped to 7.1 after 12 hrs time. These pH variations are caused by an increase of nitrification efficiency which results in acid production. Each time, the pH dropped to about 7.5, a solution of Na_2CO_3 was added to adjust it to 8.5 as it can be seen on the pH curve above (Figure 2(c)).

Towards the end of the operation, the observed rapid drop of pH was probably the consequence of a rapid oxidation of the remaining low ammonia-nitrogen by the relatively high DO concentration (around 1.5 mg/L DO concentration). The nitrification ended after 16h reaction time with a decrease of pH to nearly 6.2 (Figure 2(c)).

A successful shortcut nitrification and denitrification was achieved with a 16 h's cycle composed by 16 sub-cycles of 1h (45/15min AAA phases) at 9 L-air/min aeration rate (average DO concentration of 1.1 mg-O_2/L). The inhibition of nitrite oxidizing bacteria (NOB) in favor of AOB is the consequence of the applied aeration strategy which allows performing the operations at low DO concentrations within the SBR tank. Our results are close to the findings of Chuang *et al.* [9] which reported effective nitritation under DO concentration of 1.2 mg-O_2/L when investigating partial nitrification by implementing a closed down-flow hanging sponge (DHS) reactor in which oxygen concentration can be easily manipulated by controlling airflow to the reactor. In fact, by operating with an HRT of 1.5 h at 30˚C and 1.2 mg-O_2/L (except during the startup periods), a strong relationship between oxygen concentration and nitrite production was observed after five months of continuous operation. Their results, as in our cases, confirmed partial nitrification under oxygen limitation and the system showed a high ammonium-removal rate. Our observations are also confirmed by Bernet *et*

al. [10] which noted partial nitrification but at a very low DO concentration (0.4 mg-O_2/L) when working with a completely stirred biofilm reactor based on nitrification process under low dissolved oxygen (DO) concentration. On contrary, their influent synthetic wastewater concentration of 250 mg NH_4-N/L was lesser than ours. Their results showed a stable nitrite accumulation in the effluent after 110 days' operation with NO_2-N:(NO-N) in the effluent reaching over 90% under 0.5 mg-O_2/L while in this study both nitrification efficiency and nitritation rate were nearly 99% and the nitrate concentration was less than 3.9 mg/L. Despite a difference in DO concentration (1.1 mg-O_2/L) and inlet high ammonium-nitrogen concentration (1000 mg-NH_4-N) wastewater, our system also showed a complete ammonium conversion to nitrite as well as less than 5 mg/L NH_4-N in the outlet. As in Bernet *et al.* [10] study, the SBR intermittent aeration system shows clearly a saving in aeration cost. However, Ruiz *et al.* [11] observed that effective partial nitrification could only happened at low DO concentrations in the range of 0.5 - 1.7 mg-O_2/L contrasting with the above observations. In their cases, treating high ammonia synthetic wastewater could only yield an accumulation of at least 65% of the loaded nitrogen as nitrite when operating at a DO around 0.7 mg/L. These results are different to those recorded in this study which show nearly 99% ammonium conversion as nitrite.

On the other hand, this work has also showed the impact of 50% volume exchange ratio (VER) parameter on high ammonia-nitrogen removal as nitrite. These findings are in contrast with those by Fux *et al.* [23] which found that a stable shortcut nitrification could never be achieved with 60% VER per cycle during the start-up experimental operations under intermittent aeration patterns. However, in their work, nitritation was only achieved under operational conditions with 20% VER. In contrary to our work, only a nitrogen removal of about 85% - 90% was realized at an ammonium loading rate of 1.2 kg [corrected] NH_4^+-N $m^{-3}\cdot d^{-1}$ and more the denitritation required ethanol as electron donor a ratio of 2.2 g $COD\cdot g^{-1}$ N removed. Lai *et al.* [24], using the laboratory scale SBR process concept achieved complete nitrogen removal through nitritation and denitritation with a total reduction of 96% - 98% of the ammonium nitrogen from biosolids dewatering liquids (influent concentration typically 1200 $g\cdot m^{-3}$) with a short HRT of 1.1 d and a removal rate of 1.05 $kgNm^{-3}d^{-1}$. Their experimental ammonium nitrogen removal results seem close to those observed in this study.

3.2. Comparative Study of the Effects of Aeration Rates on Shortcut Nitrification and Denitrification

All the operations were conducted within the intermittently aerated SBR with influent of 1000 mg/L ammonia-nitrogen concentration and 50% VER. All the SBR's 16 h cycles involved 16 sub-cycles composed by identical aeration pattern of 45/15-min AAA phases each. Successive aeration rates of 3, 6, 9, 12 and 15 L-air/min were separately applied to the SBR operations.

Figure 3 below shows the effluents' NH_4-N, NO_3-N and NO_2-N concentrations of different cycles at 3, 6, 9, 12 and 15 L-air/min aeration rates corres-

ponding to average DO concentrations of 0.2, 0.8, 1.1, 1.4 and 1.7 mg-O_2/L, respectively. Under operations with 3 and 6 L/min aeration rates, the effluents NH_4-N concentrations remain as high as 321.6 and 183.8 mg-NH_4-N/L, respectively (Table 3, Figure 3). The ammonia-nitrogen oxidation to nitrite is incomplete in the two cases (see Figure 4(a) and Figure 4(b) below). The ammonia-nitrogen conversion to nitrite was affected as depicted in Table 3 below with only 35.7% and 63.0% nitrification efficiencies, respectively.

However, at 9 L-air/min aeration rate (average DO of 1.1 mg-O_2/L), about 99% both nitrification efficiency and nitritation rate (Table 3, Figure 3) were obtained with only 2.6 mg/L NO_3-N concentration while denitrification rate is around 25.9%. Figure 4(c) shows a profile of the complete oxidation of ammonia to nitrite at 9 L-air/min under 45/15-min AAA phases. When operating at 12 L-air/min (average DO of 1.4 mg-O_2/L), the ammonia-nitrogen conversion is not affected, and both nitrification efficiency and nitritation rate still remain around 98.9% but denitrification rate is about 34.7% (Table 3, Figure 3). In

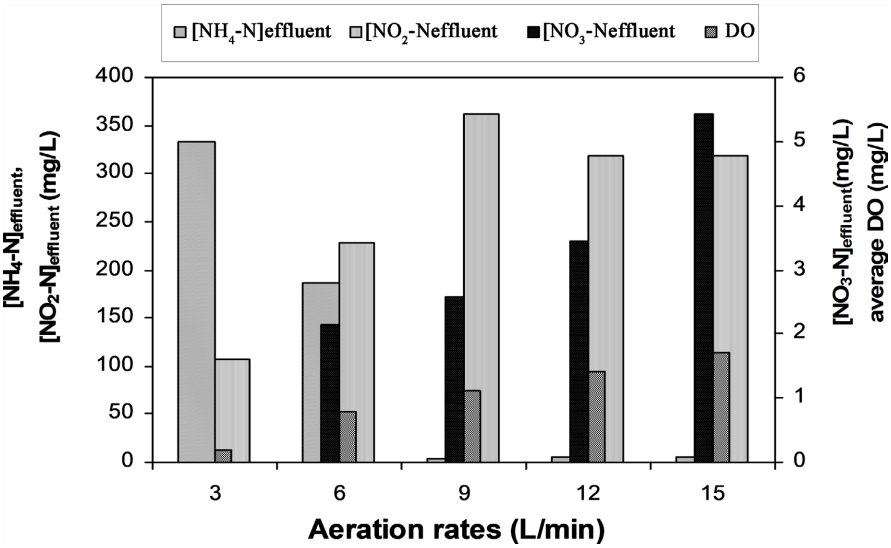


Figure 3. Profiles of effluents' NH_4-N, NO_3-N and NO_2-N concentrations and average DO concentrations at different aeration rates.

Table 3. Nitrification efficiency and nitritation rate at different aeration rates.

Aeration rates (Lair/min)	Effluent concentrations (mg/L)			Nitrification efficiency (%)	Nitritation rate (%)	Denitrification rate (%)
	NH_4-N	NO_2-N	NO_3-N			
3	321.6	127.9	2.7	5.7	97.9	9.5
6	183.8	228.4	2.2	63.0	98.9	17.1
9	3.4	279.4	2.6	99.1	99.0	25.9
12	3.4	319.1	3.5	99.3	98.9	34.7
15	lower than the detection limit	319.2	5.4	100.0	98.3	35.1

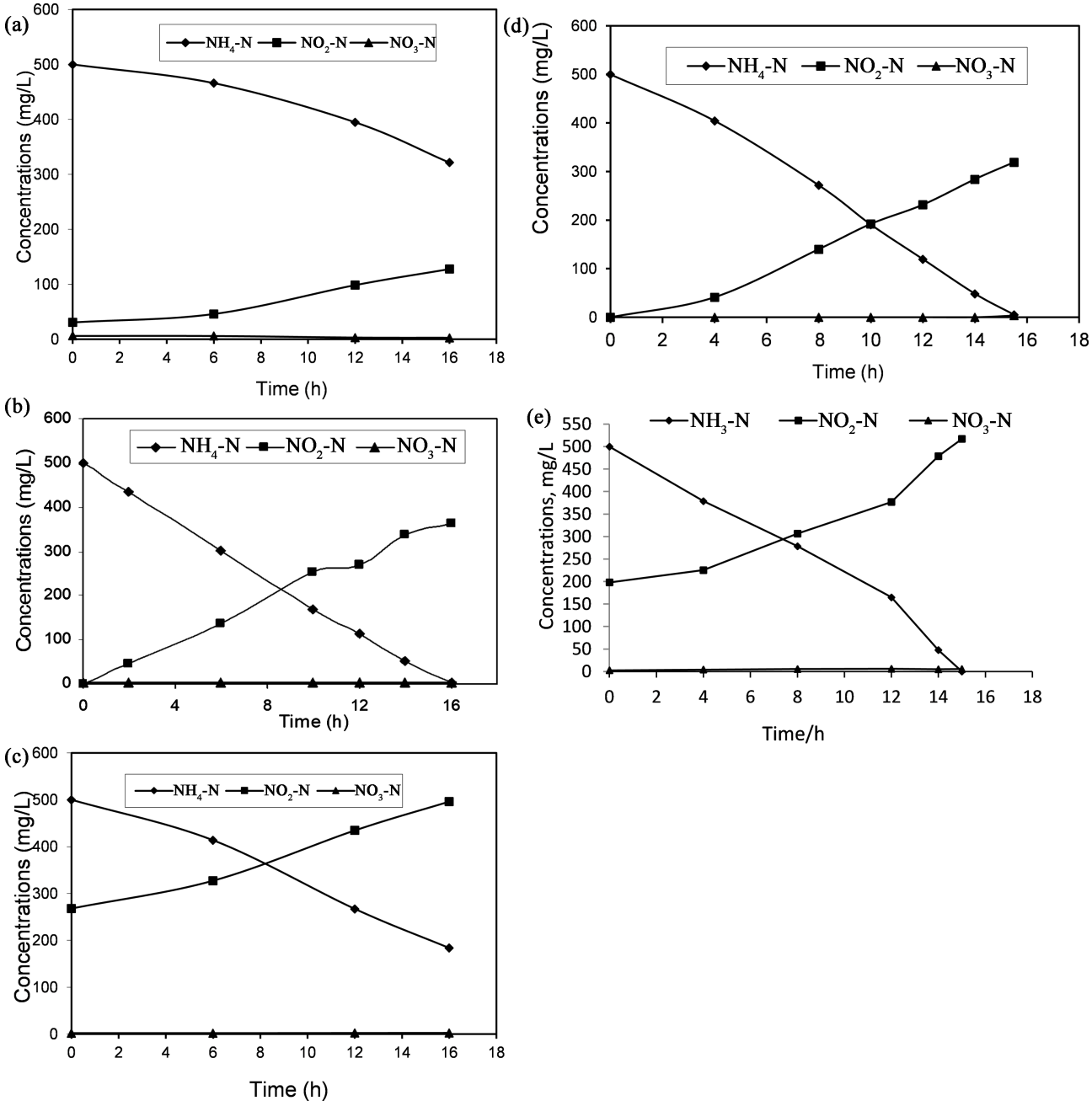


Figure 4. Some complete SBR 16 h cycle profiles of NH_4^+-N, NO_2^--N and NO_3^--N at aeration rates of 3, 6, 9, 12, and 15L-air/min under 45/15-min AAA phases. (a) 3 L-air/min, 45/15-min AAA phases; (b) 6 L-air/min, 45/15-min AAA phases; (c) 9 L-air/min, 45/15-min AAA phases; (d) 12 L-air/min, 45/15-min alternate aerobic/anoxic; (e) 15 L-air/min, 45/15-min AAA phases

addition, the complete ammonia-nitrogen oxidation to nitrite's cycle duration decreases from 16 h to 15.5 h (**Figure 4(d)**) while the effluent NO_3-N concentration remains less than 5 mg/L. At 15 L-air/min aeration rate (*i.e.* average DO of 1.7 mg-O_2/L), the shortcut nitrification still persist along with a decrease in ammonia-nitrogen oxidation to nitrite's cycle duration which drops again to 15 h (**Figure 4(e)**). However, the effluent NO_3-N concentration starts to rise over 5 mg/L while the denitrification remains poor as showed in **Table 3**.

Complete ammonia-nitrogen conversion to nitrite could never be obtained under average DO concentration of 0.2 mg-O_2/L with considered 45/15 AAA aeration pattern. In this operation, both AOB and NOB are probably affected due to DO depletion and the high ammonia-nitrogen concentration. This result is in accordance to the findings of Ruiz *et al.* [10] which noted that under DO concentration below 0.5 mg-O_2/L, ammonia was accumulated meaning no nitrite accumulation was observed. Even when operating at 0.8 mg-O_2/L concentration, ammonia still accumulated in the effluent wastewater which contrasts to the findings of Ruiz *et al.* [10] which found that it is possible to achieve an accumulation of at least 65% of the loaded nitrogen as nitrite when operating at a DO around 0.7 mg/L. However, at average DO concentrations of 1.1 and 1.4 mg-O_2/L, both nitrification efficiency and nitritation rate are above 99% and 98% respectively. This result is also observed even at 1.7 mg-O_2/L concentration. In conclusion, under conditions of above DO concentrations and aeration pattern, ammonia conversion to nitrite was achieved. These results are better than those obtained by Antileo *et al.* [29] whose results are nitrite accumulations of 84% - 88% during long-term assays, and a relatively high ammonia conversion rate of 1.45 - 4.25 kg NH_4^+-N/(m^2 day). In addition, in their cases when decreasing the oxygen concentration from 1.0 to 0.8 mg O_2/L, the ammonium removal rate declined significantly from 4.25 to 1.62 kg/(m^2 day) which contrasted to our findings. On the other hand, the low denitrification rates obtained during all these operations were probably due to the high nitrite concentration in the bulk water along with a possible trapping of nitrogen gas inside sludge flocs.

In this study, the operational pH was adjusted between 7.5 and 8.5 and temperature controlled to 25˚C ± 2˚C resulting in FA concentration of 5.4 - 58.7 mg/L. These FA concentrations are between the values which normally must inhibit both NOB and AOB activities as stated by the research of Anthonisen *et al.* [30] whose results showed that FA concentrations of 0.1 - 1.0 mg/L inhibited NOB while 10 - 150 mg/L inhibited AOB. In the present study, NOB was completely inhibited by high FA concentrations confirming the above hypothesis, however, AOB activity was not affect. This is in accordance with the work by Cecen and Gonenc [31] which noted the combined effect of high ammonia and high pH of 8.5 conditions inhibited NOB and led to partial nitrification.

It could be possible to achieve stable shortcut nitrification and denitrification process by combining the effects of aeration rate (moderate DO concentrations), operational aeration strategy and high FA concentration and this is a confirmation of the previous observation made by Daniel *et al.* [32] when treating two distinct ammonia concentrations of 125 and 250 mg/L during cycles of 24 h under intermittent aeration for periods of 1 h and ethanol used as a carbon source at the beginning of each anoxic period.

3.3. Effects of Aeration Patterns on TN Removal

Figure 5 below presents the SBR performance during operations with cycle

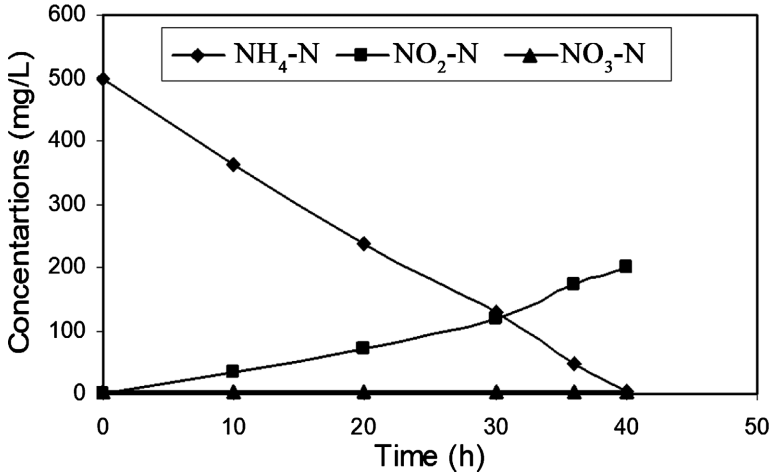


Figure 5. Cycle profiles of NH_4-N, NO_2-N and NO_3-N with sub-cycles of 15/45min AAA phases.

comprising 15/45min AAA phases at experimental conditions of 9 L-air/min aeration rate, temperature of 25˚C ± 2˚C, pH ranged between 7.5 - 8.5 and 50% VER. It can be seen that the ammonia-nitrogen oxidation to nitrite is achieved in 40 h.

The above Table 2 shows the effluents' concentrations corresponding to NH_4-N, NO_2-N and NO_3-N concentrations, respectively. When comparing the TN removal rates during the two different cycles composed by 45/15 and 15/45min AAA phases, it appears in Table 2 that the TN removal rates are 25.9% and 58.6% for the cycles composed by sub-cycles of 45/15min AAA phases and 15/45min AAA phases, respectively. According to these results, the TN removal efficiency is better during operations with sub-cycles of 15/45min AAA phases than with 45/15min AAA phases. This difference can be associated to the long anoxic phase during the operations under sub-cycle of 15/45min AAA (15 min aeration against 45 min anoxic) which induced better denitritation stage than with the cycle including sub-cycle of 45/15min AAA phases (only 15 min aeration phase against 45 min anoxic period).

Table 4 below shows the results of SBR operations with 24 h cycle composed by sub-cycles of 50/40min (alternating 50 min aeration and 40 min anoxic phases) and 40/50min (intermittent 40min aeration and 50 min anoxic phases) AAA phases. The results showed complete ammonia-nitrogen oxidation to nitrite with effluents' NH_4-N concentrations of 3.3 mg/L with cycle of 50/40min AAA phases while recording effluent's NH_4-N concentration of 4.5 mg/L with cycle of 40/50min AAA phases. Meanwhile, with sub-cycles of 50/40min AAA phases 99.3% and 99.0% nitrification efficiency and nitritation rate, were obtained respectively. Whereas, operations with 40/50min AAA phases sub-cycles give 99.1% nitrification efficiency and 98.6% nitritation rate. In both cases, less than 2.3 mg/L NO_3-N concentrations are recorded meaning the system works as a shortcut nitrification and denitrification process. On the other hand, based on the results of Table 4, it appears that the nitrite production is higher with cycle

of 50/40min AAA phases than with sub-cycle of 40/50min AAA phases. Whereas the cycle with 40/50min AAA phases shows better TN removal rate of 71.5% than cycle with 50/40min AAA phases with 52.9% TN removal rate. This can be probably the consequence of the long anoxic phase of the denitritation stage during the cycle with 40/50min AAA phases which favors high TN removal.

Figure 6(a) & Figure 6(b) below present the complete cycles' profiles of NH_4-N, NO_2-N and NO_3-N during operations at 9 L-air/min aeration rate with 24 h cycles composed by sub-cycles of 50/40min and 40/50min AAA phases. It can be seen clearly that in both cases the NO_3-N concentrations were less than

Table 4. TN removals under sub-cycles of 50/40 and 40/50min during 24 h cycles.

Parameters patterns min	Intermittent aeration	
	50/40 min	40/50
$[NH_4\text{-}N]_{effluent}$ (mg/L)	3.3	4.5
$[NO_2\text{-}N]_{effluent}$ (mg/L)	2.3×10^2	1.3×10^2
$[NO_3\text{-}N]_{effluent}$ (mg/L)	2.3	2.0
Nitrification efficiency (%)	99.3	99.1
Nitritation rate (%)	99.0	98.6
TN removal rate (%)	52.9	71.5

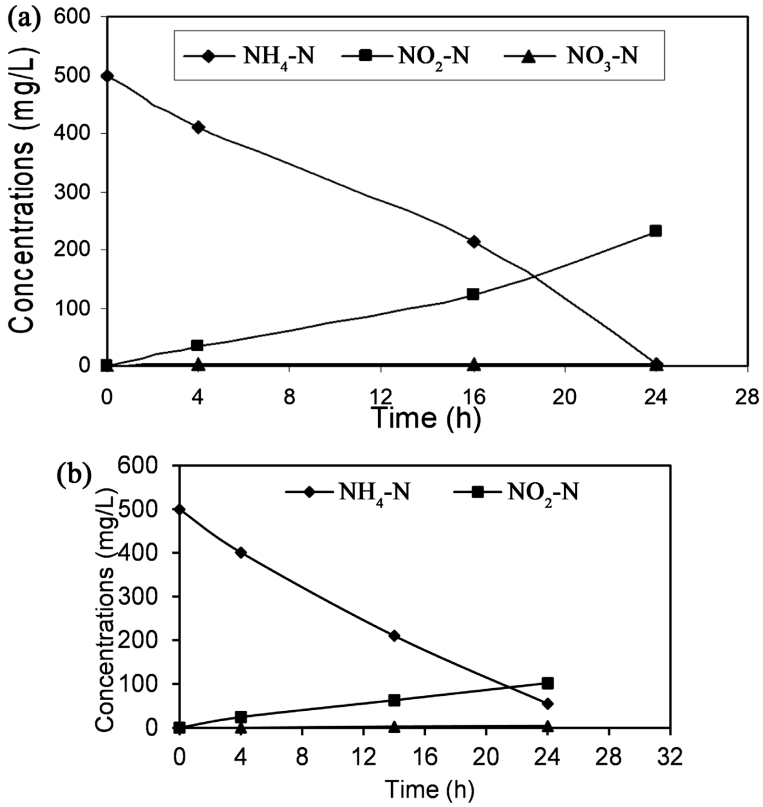


Figure 6. Cycle profiles of NH_4-N, NO_2-N and NO_3-N at 50/40min AAA (a) and 40/50min AAA (b) during 24 h cycle.

2.3 mg/L. Moreover, ammonia-nitrogen removal to nitrite route is effective under sub-sub-cycle of 50/40min AAA phases but when working with sub-cycle of 40/50min AAA phases about 3.3 mg/L NH_4-N concentration is recorded. The difference in nitrite concentrations can be related to the aeration pattern which confirms the above hypothesis which has noted better TN removal during cycle with 40/50min AAA phases than with 50/40min AAA phases.

From these comparative studies, it can be concluded that operations with cycle involving sub-cycle with long anoxic phase (non-aeration phase) gives the best TN removal. In addition, when comparing operations with sub-cycles of 15/45 and 40/50min AAA phases, it appears that the best TN removal of 71.5% is obtained when operating under the latter condition. Therefore, relatively high TN removal efficiency has been achieved by operating with sub-cycle comprising long anoxic phase over aerobic phase with respect to nitrification efficiency. This result is in contrast to the research by Lim *et al.* [33] which observed that during operations with 2 h/cycle aeration on/off time for 12 cycles in three variations of 60/60min, 50/70min, and 40/80min, more than 82% TN removal rate was obtained, and the reactor's non-aeration time (off) should be more than 70 min while aeration time is 50 min (on). However, our results are close to Chang *et al.* [34] which observed about 72.23% TN rate in a study involving simultaneous shortcut nitrification and denitrification (SND) when treating low COD/N ratio (~x223C 4: 1) wastewater.

4. Conclusions

Lab-scale SBR shortcut nitrification/denitrification biological process was useful to perform high concentration of 1000 mg/L ammonium-nitrogen (NH_4-N) oxidation via nitrite route at different DO concentrations under various intermittent aeration patterns.

A complete NH_4-N oxidation to nitrite was effective at 1.1 mg-O_2/L (*i.e.* 9 L-air/min) showing with 99.1% nitrification efficiency, 99.0% nitritation rate and 2.6 mg- NO_3^--N/L nitrate concentration.

The best results during first operations were obtained at 1.4 mg-O_2/L (*i.e.* 12 L-air/min) showing 99.3% nitrification efficiency and about 98.9% nitritation rate while nitrate concentration remains about 3.5 mg- NO_3^--N/L. By comparing these assessments, it results that the nitrite accumulation rate was related to DO concentration and cycle's duration. Nevertheless, the DO amount needs to be controlled in order to avoid the return to conventional nitrification/denitrification process. In fact, at 1.7 mg-O_2/L (*i.e.* 15 L-air/min), the system showed an increase in nitrate concentration with more than 5 mg/L which could be a point of reverse to conventional nitrification.

The second operations gave the best total nitrogen (TN) removal rate when working under 1.5 hours' sub-cycle operations with 71.5% TN removal under operations with 40/50 min AAA pattern. Thus, during SBR's shortcut nitrification and denitrification operations, intermittent aeration pattern with long anoxic

period over short aeration period ensured the best TN removal.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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