



Optimisation for Enriching Ammonium Oxidizing Bacteria in Membrane Partial Nitrification Reactor: Mathematical Simulation

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ABSTRACT

Partial nitrification is thought to be a more economical process for the removal of high ammonia concentration from wastewater. In order to promote nitrite accumulation, the key step is to take measures to enrich ammonia oxidizing bacteria (AOB) and suppress nitrite oxidizing bacteria (NOB) in a membrane biological reactor (MBR). Using a mathematical model, the effects of different operational parameters, such as dissolved oxygen (DO), sludge retention time (SRT) and temperature et al., have been evaluated in terms of the nitrification process. The results indicated that DO could be used as an independent control factor to achieve partial nitrification. High temperature and low SRT were shown to be advantageous for AOB accumulation, and a low SRT was shown to decrease the sensitivity of partial nitrification to variations in DO concentration. The successful start-up partial nitrification process is more stable with a combination of various parameters, such as DO and influent concentration. Low temperature causes ammonia accumulation due to the decreased metabolic activity of AOB. By increasing DO concentration, it is possible to maintain a stable system despite seasonal temperature changes. It was clarified that a suitable combination of DO and other parameters is crucial achieving a partial nitrification process.

Keywords: Partial nitrification; AOB; NOB; mathematical model; simulation

1. INTRODUCTION

Since the excess discharge of ammonia from wastewater is the main cause of eutrophication, which leads to harmful algal blooms and hypoxia in ocean and freshwater (Howarth and Marino, 2006), efficiently eliminating nitrogen from ammonium-rich wastewater is one of the biggest challenges in the field of wastewater treatment technology. Conventional nitrification-denitrification biological processes often are not appropriate for the low

C/N wastewaters because of the high energy requirement for aeration and the lack of sufficient electron donors. Therefore, new technologies have been developed, such as the complete autotrophic nitrogen removal over nitrite (ANNON) (Sliemers et al., 2003; Third et al., 2005) and shortcut nitrification and denitrification (Gao et al., 2009; Yoo et al., 1999), combining the high ammonia removal over the nitrite process (SHARON) with anaerobic ammonia oxidation (ANAMMOX) (Hwang et al., 2005; van Dongen et al., 2001),

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have been developed. In most of these new technologies, successfully achieving the stable partial nitrification to nitrite is the key.

In the process of aerobic ammonium oxidation, two different groups of bacteria are involved. Ammonia oxidizing bacteria (AOB) convert ammonia to nitrite and then nitrite oxidizing bacteria (NOB) oxidize nitrite to nitrate. Therefore, in order to accumulate nitrite in the reactor, the key is to take measures to enrich the AOB and suppressor inhibits NOB. A variety of operational parameters or combinations of them have been controlled to achieve the partial nitrification to nitrite, due to their different effects on the AOB and NOB kinetics (Peng and Zhu, 2006).

Because the minimum doubling time of AOB and NOB is 7-8 h and 10-13 h, respectively, a short sludge retention time (SRT) is an obvious advantage to enrich AOB and wash out NOB in a suspended-growth system, which was verified in the SHARON process using less than 2 days of SRT to accumulate nitrite (van Kempen et al., 2001). However, recent studies have indicated that it is also feasible to successfully achieve the partial nitrification under a long sludge age (Pollice et al., 2002; Torà et al., 2012). The control of the dissolved oxygen (DO) concentration in the reactor was often used to attain partial nitrification (Blackburne et al., 2008; Wang and Ning, 2004). Although free ammonia (FA) is considered the real reactive substrate in the nitrifying process, a higher FA concentration can inhibit the activities of AOB and NOB, and cause more serious inhibition on NOB than on AOB (Chen et al., 2010; Zhang et al., 2012; Zhou et al., 2011). Therefore, FA and free nitrous acid (FNA) also can be used to promote nitrite accumulation because the range of inhibition thresholds reported showed that NOB is more sensitive to FNA than AOB (Xue et al., 2009). Furthermore, temperature affects the growth rate of both AOB and NOB, with the

growth rate of AOB faster than that of NOB. At temperatures higher than 25°C, AOB has been shown to out-compete NOB because of AOB's higher increase of growth rate (Hellings et al., 1998; Sinha and Annachhatre, 2007). Since pH regulates the equilibrium between NO_2^- and FNA as well as NH_4^+ and FA, at $\text{pH} > 7$ the effect is doubled: not only does it limit the conversion of NO_2^- into FNA, which inhibits nitrifiers, it also ensures the concentration of FA that selectively inhibits NOB and therefore leads to the stability of partial nitrification (Pollice et al., 2002).

Modeling is a powerful tool for a researcher to test the understanding of the metabolic kinetics of microorganisms. The explicitly quantitative nature of a model gives structure to a conceptual understanding, and it also allows a rigorous evaluation of the understanding against experimental results (Price, 2011; Qi et al., 2014). Systematic analysis of the independent and interactive effect of operational parameters on partial nitrification should be carried out to control the various operational parameters to attain partial nitrification. In this article, the kinetic model of ammonia oxidized was used to evaluate the effects and sensitivities of operational parameters for partial nitrification process.

2. MATERIALS AND METHODS

2.1 Model construction

Assuming a constant volume membrane biological reactor (MBR) with a well-mixed tank, and the sludge could be kept in the reactor by sludge pump according to the SRT (Fig. 1). A reliable design model for nitrification performance must be able to estimate the growth rates of the ammonium oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB).

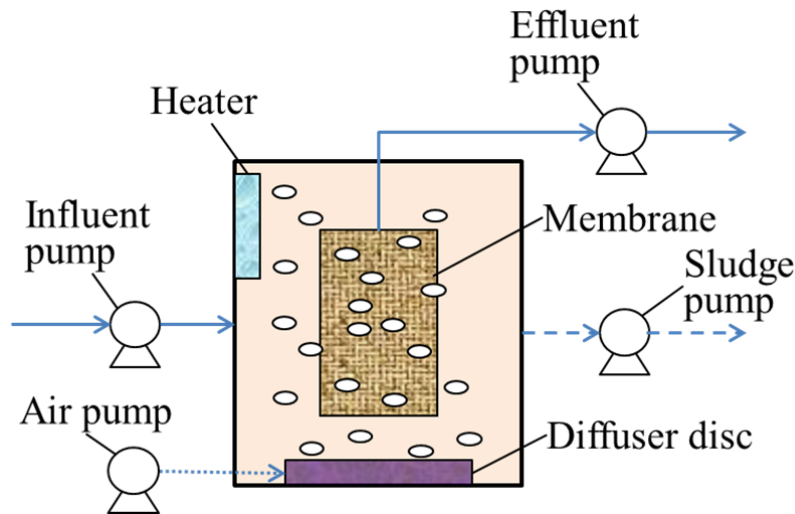


Figure 1 Diagram of the reactor system for the simulation

The model mainly considers the kinetics of substrate degradation and is adapted from Activated Sludge Model No. 1 (ASM1). In particular, the model takes six components (substrates and products): ammonia (S_{NH_4} , g-N/m³), nitrite (S_{NO_2} , g-N/m³), nitrate (S_{NO_3} , g-N/m³), AOB (X_{AOB} , g-COD/m³), NOB (X_{NOB} , g-COD/m³) and residual inert biomass (X_I , g-COD/m³). All quantitative models are based on mass conservation (Kissel et al., 1984). Then, the variation in the mass of a dissolved or particulate component with time for the system can be written as follows:

$$\frac{dC}{dt} = \frac{1}{RT} C_{\text{in}} - \frac{1}{RT} C + r \quad (1)$$

Where C is the component concentration in the reactor; C_{in} is the component in the influent; t is the time; RT is the hydraulic retention time (S_{NH_4} , S_{NO_2} and S_{NO_3}) or sludge retention time (X_{AOB} , X_{NOB} and X_I); and r is the reaction rate.

Monod-type expressions are used to describe the rates of the biochemical elimination and transformation processes. The equation below describes the overall reaction rate in terms of the bulk liquid substrate concentration (S):

$$-\frac{dS}{dt} = \mu_{\text{max}} \frac{S}{K+S} X \quad (2)$$

Where X is the mass of bacteria; K and μ_{max} denote the half-velocity constant and maximum specific growth rate, respectively, which parameterize the biological reaction rate alone. This equation provides an approximate description of the variation in the substrate flux with the bulk liquid concentration.

A reliable design model for nitrification performance must be able to estimate the growth rates of the ammonium oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). The process involves two sequential steps. This model was based on several assumptions.

The biological reactor is a completely stirred tank reactor (CSTR);

The degradation of each substrate proceeds according to Monod kinetics.

The affinity constants are not accurately known. Therefore, attention should be focused on the effect of affinity constants on the process performance.

There are inhibitions of FA on the bacteria.

The model mainly considers the kinetics of

substrate degradation. In particular, the model takes six components (substrates and products); ammonia (S_{NH_4} , g-N/m³), nitrite (S_{NO_2} , g-N/m³), nitrate (S_{NO_3} , g-N/m³), AOB (X_{AOB} , g-COD/m³), NOB (X_{NOB} , g-COD/m³) and residual inert biomass (X_I , g-COD/m³). There is competition between the three autotrophic organisms for oxygen, nitrite, and ammonium, respectively. The relevant stoichiometric coefficients and process rate expressions have been incorporated in Table 1.

2.2 Parameter setting and numeric integration

The effective volume of the simulated reactor was set as 1 m³. The models used in this study were state of the art models for wastewater treatment. The kinetic and stoichiometric parameter values are shown in Table 2. The initial mixed liquor volatile suspended solids (MLVSS) were set as 2250 mg/L, respectively. The initial AOB and NOB concentrations were set as 100 and 200 mg/L because the ratio of AOB and NOB in the active sludge of urban sewage treatment plants was in the range of 3% to 5% (Guo et al., 2009). Numeric integration of the differential equations is performed using the solving algorithm ode45 solver based on

the numerical differentiation formulas in the software Matlab/Simulink[®]. A gradient descent is used as the optimization method.

3. RESULTS AND DISCUSSION

3.1 Effect of DO Concentration on the nitrification process

The effects of DO concentration on the accumulation of nitrite were investigated. As shown in the Fig. 2, the accumulation of nitrite could not be achieved due to the rapid conversion of nitrite to nitrate when DO concentration was 0.5 mg/L. When DO concentration was between 0.1 and 0.2 mg/L, partial nitrification could be attained, but stability in the higher DO system and takes longer time. Even though the metabolic activities of AOB maybe decrease in low DO concentration (Hidaka et al., 2002). It can be seen that DO could be used as a control factor to achieve partial nitrification. However, when DO concentration is too low, then nitrification process is not feasible because the metabolic activity of AOB is much low at a DO concentration of 0.05 mg/L. Therefore, aeration cost can be reduced by using DO as a control parameter to achieve the accumulation of nitrite (Peng and Zhu, 2006).

Table 1 Stoichiometric matrix and process kinetic rate equations for the aerobic processes model

→i	1	2	3	4	5	6	7	Kinetics rates expressions
↓j	S_{O_2}	S_{NH_4}	S_{NO_2}	S_{NO_3}	X_{AOB}	X_{NOB}	X_I	
1 Growth of AOB	-	$-\frac{1}{Y_{\text{AOB}}}$	$-i \frac{1}{Y_{\text{AOB}}}$	-	1	-	-	$\mu_{\text{AOB}} \frac{S_{\text{NH}_4}}{K_{\text{NH}_4}^{\text{AOB}} + S_{\text{NH}_4}} \frac{S_{\text{O}_2}}{K_{\text{O}_2}^{\text{AOB}} + S_{\text{O}_2}} X_{\text{AOB}} I_{\text{FA}}^{\text{AOB}} I_{\text{FNA}}^{\text{AOB}}$
2 Decay of AOB	-	$i(1-d)$	-	-	-1	-	d	$b_{\text{AOB}} X_{\text{AOB}}$
3 Growth of NOB	-	$-i$	$-\frac{1}{Y_{\text{NOB}}}$	$\frac{1}{Y_{\text{NOB}}}$	-	1	-	$\mu_{\text{NOB}} \frac{S_{\text{NO}_2}}{K_{\text{NO}_2}^{\text{NOB}} + S_{\text{NO}_2}} \frac{S_{\text{O}_2}}{K_{\text{O}_2}^{\text{NOB}} + S_{\text{O}_2}} \frac{S_{\text{NH}_4}}{K + S_{\text{NH}_4}} X_{\text{NOB}} I_{\text{FA}}^{\text{NOB}} I_{\text{FNA}}^{\text{NOB}}$
4 Decay of NOB	-	$i(1-d)$	-	-	-	-1	d	$b_{\text{AOB}} X_{\text{AOB}}$

$$\left\{ \begin{aligned}
 I_{FA}^{AOB} &= \frac{K_{FA}^{AOB}}{K_{FA}^{AOB} + \frac{S_{NH4} \times 10^{pH}}{6334} e^{273+T} + 10^{pH}}, I_{FA}^{NOB} = \frac{K_{FA}^{NOB}}{K_{FA}^{NOB} + \frac{S_{NH4} \times 10^{pH}}{6334} e^{273+T} + 10^{pH}} \\
 I_{FNA}^{AOB} &= \frac{K_{FNA}^{AOB}}{K_{FNA}^{AOB} + \frac{S_{NO2}}{e^{273+T} \times 10^{pH}}}, I_{FNA}^{NOB} = \frac{K_{FNA}^{NOB}}{K_{FNA}^{NOB} + \frac{S_{NO2}}{e^{273+T} \times 10^{pH}}} \\
 \mu_{AOB} &= \mu_{AOB}^{30^{\circ}C} (1 + (T - 30) * \frac{1 - \frac{1}{20}}{5.3}), \mu_{NOB} = \mu_{NOB}^{30^{\circ}C} (1 + (T - 30) * \frac{1 - \frac{1}{20}}{2.6})
 \end{aligned} \right.$$

Table 2 Kinetic and stoichiometric parameter values used in this work

Parameter	Definition	Values	Unit	Source
<i>Stoichiometry</i>				
Y_{AOB}	yield coefficient for AOB	0.150	g-COD _x /g-N	This study
Y_{NOB}	yield coefficient for NOB	0.041	g-COD _x /g-N	This study
i	Nitrogen content of biomass	0.07	g-N/g-COD _x	(Gujer et al., 1999)
d	fraction of X_i in biomass decay	0.08	g-COD _x /g-COD _x	(Henze et al., 1987)
<i>Kinetics</i>				
μ_{AOB}	maximum growth rate of AOB at 30°C	2.05	1/d	(Wiesmann, 1994)
μ_{NOB}	maximum growth rate of NOB at 30°C	1.45	1/d	(Wiesmann, 1994)
b_{AOB}	death rate coefficient of AOB	0.13	1/d	(Wiesmann, 1994)
b_{NOB}	death rate coefficient of NOB	0.06	1/d	(Wiesmann, 1994)
K_{NH4}^{AOB}	saturation constant for S_{NH4} of AOB	2.4	g-N/m ³	(Wiesmann, 1994)
K_{NO2}^{NOB}	saturation constant for S_{NO2} of NOB	5.5	g-N/m ³	(Wiesmann, 1994)
K_{O2}^{AOB}	saturation constant for S_O of AOB	0.6	g-O ₂ /m ³	(Wyffels et al., 2004)
K_{O2}^{NOB}	saturation constant for S_O of NOB	2.2	g-O ₂ /m ³	(Wiesmann, 1994)
K	switching constant for S_{NH4}	0.01	g-N/m ³	-
K_{FA}^{AOB}	Inhibition constant of NH ₃ on AOB	241	g-N/m ³	(Pambrun et al., 2006)
K_{FA}^{NOB}	Inhibition constant of NH ₃ on NOB	11.1	g-N/m ³	(Pambrun et al., 2006)
K_{FNA}^{AOB}	Inhibition constant of HNO ₂ on AOB	0.053	g-N/m ³	(Pambrun et al., 2006)
K_{FNA}^{NOB}	Inhibition constant of HNO ₂ on NOB	3.9	g-N/m ³	(Pambrun et al., 2006)

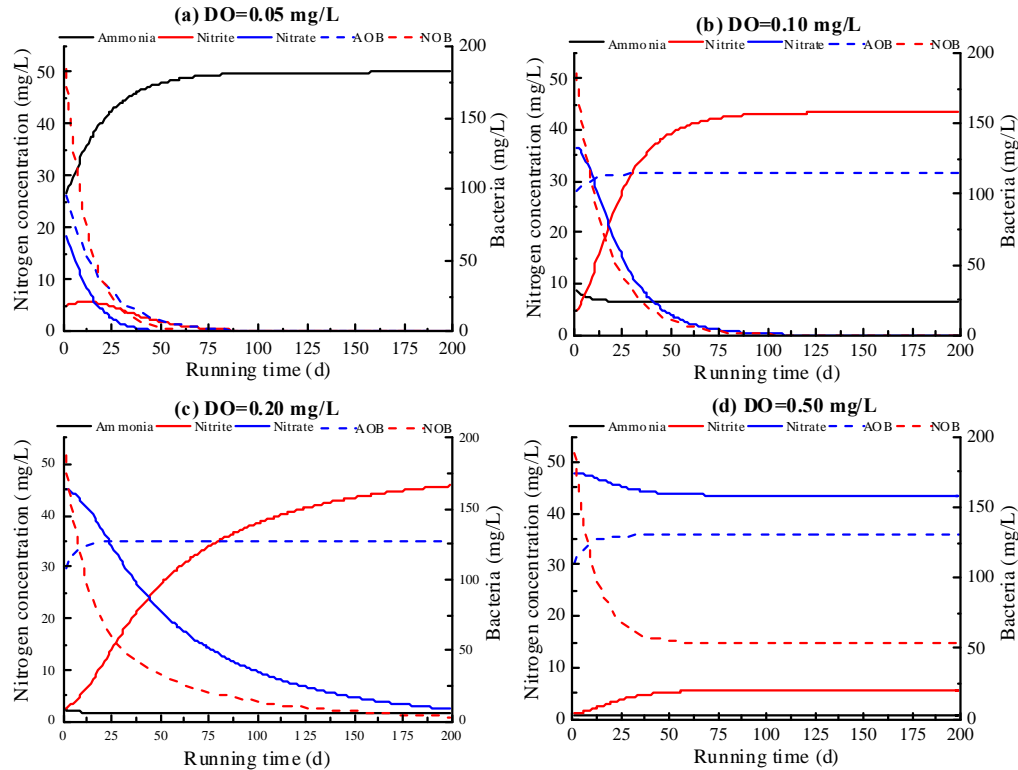


Figure 2 Effects of different DO concentration on nitrification process under the conditions of pH = 7.0, T = 25°C, initial $\text{NH}_4^+\text{-N}$ = 50 mg/L and SRT = 20 d

3.2 Effect of SRT on the nitrification process

SRT was shown to have a significant effect on the nitrification process as shown in the steady state results of nitrification at different SRTs in Fig. 3. This study indicated that using the SRT as a factor to achieve partial nitrification is possible except when DO concentration was accurately controlled. Moreover, a lower SRT had the advantage of accelerating the start-up of partial nitrification.

With decreasing SRT values, the biomass of AOB and NOB also decreased due to the washout from reactor with effluent, which may result in a lower ammonia conversion rate. In order to avoid this, it is necessary to adopt strategies to increase the multiplication or metabolic activity of AOB (Torà et al., 2012). When the long sludge stage (over 5 days) was used, partial nitrification can also be attained by control the DO between 0.2-0.7 mg/L.

When the SRT was set at 1 d, it was possible to achieve partial nitrification. However, a lower SRT means the high demand for DO concentration for the complete oxidation of ammonia.

3.3 Effect of temperature on the nitrification process

Our simulation indicates that partial nitrification is affected by temperature as can be seen in Fig. 4. The metabolic activities of AOB increased with increasing temperature. Partial nitrification can also be attained when the temperature of the system is lower than 20°C only if when DO concentration is high.

Controlling the temperature was used as a means to enrich AOB and wash out NOB because the specific growth rates of AOB and NOB have different sensitivities to variations of temperature (Hellings et al., 1998; Kim et al., 2008; Peng and Zhu, 2006). It was concluded that although increasing the

temperature can importantly affect the specific growth rates of AOB and NOB, temperature should connect with DO as control measure for attaining partial nitrification.

3.4 Effect of FA and FNA on the nitrification process

The effects of FA and FNA on the nitrification process were studied by changing the pH value from 6.5 to 8.5. The results were shown in Fig. 5. Partial nitrification can be achieved at initial FA-N concentrations between 2.92 and 27.75 mg/L, and the successful startup time was shorter than that when the FA-N concentration was 0.3 mg/L, as can be seen in Fig. 2b. This indicates that optimizing the FA-N concentration for partial nitrification is effective because the NOB is more inhibited by FA than AOB. The rate of ammonia oxidation decreased with the increasing FA-N concentration, and that the nitrifying activity was completely inhibited when the FA concentration was 78.35 mg/L.

Moreover, higher concentration of FNA also can cause more serious effects on NOB than AOB, as was shown in Fig. 5a, which indicated that high concentration of FNA can also be as an important factor to accumulate nitrite in nitrifying process.

However, the use of FA or FNA as a decisive control factor for partial nitrification is not feasible, as shown in Fig. 6. Although the ammonia oxidation rate was importantly decreased at a DO concentration of 0.1 mg/L and an initial FA-N concentration of 78.35 mg/L and FNA-N concentration of 0.16 mg/L, partial nitrification can be attained when DO concentration was 0.2 mg/L and complete nitrification took place when DO concentration was 0.5 mg/L. It has been reported that a stable partial nitrification process was not enough because of the acclimation of NOB to high FA or FNA concentration with time (Ford et al., 1980; Han et al., 2003). Even so, the control of FA or FNA is helpful in the start-up stage.

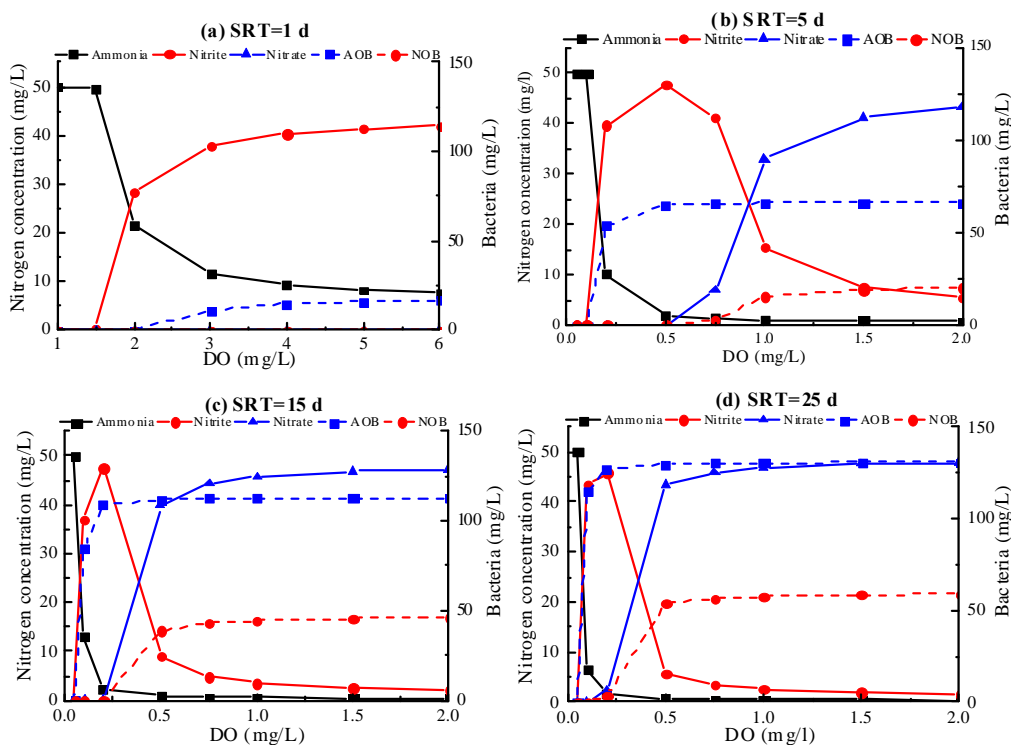


Figure 3 Effects of SRT on the nitrification process at different DO concentrations under the conditions of pH = 7.0, T = 25°C, initial $\text{NH}_4^+\text{-N}$ = 50 mg/L

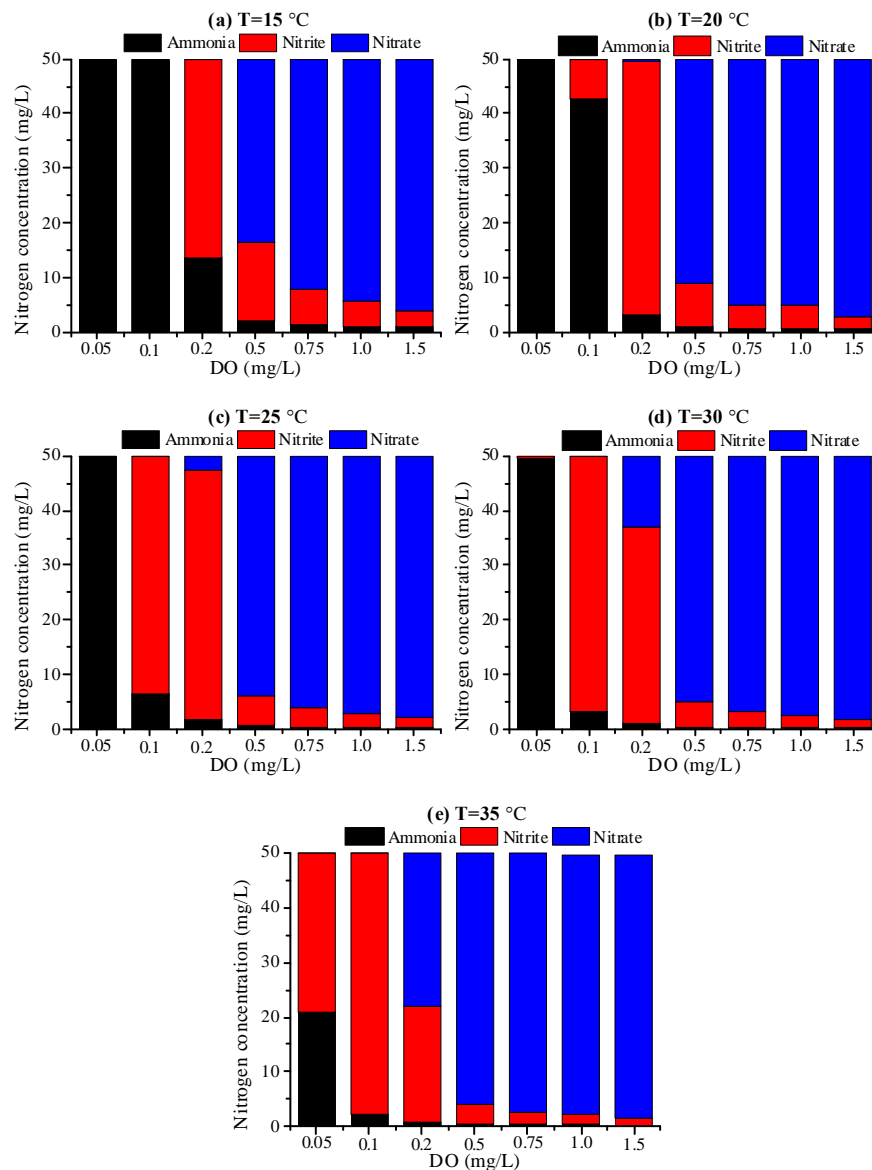


Figure 4 Steady state results of effects of temperature on the nitrification process at different DO concentrations under the conditions of $\text{pH} = 7.0$, $\text{SRT} = 20$ d and initial $\text{NH}_4^+\text{-N} = 50$ mg/L

3.5 The long-term stability of the partial nitrification

The stability of the nitrification process was analyzed by changing the each operational condition for 3 days and then recovers to initial conditions. The variation amplitude of DO and pH, and initial ammonia concentration was ± 0.5 mg/L, ± 0.5 and ± 250 mg/L, respectively. From Fig. 7, it can be seen that DO and pH and initial ammonia concentra-

tion did not have a marked effect on the partial nitrification process because of the almost complete washout of NOB from the system in the start-up stage of partial nitrification. These results were consistent with those reported by Guo et al. (2009). This implies that the partial nitrifying process remains stable and is not susceptible to the shock of parameter variation over short periods of time.

Due to a change in wastewater temperature with the season change, the effect of temperature change on the stability of partial nitrification was also evaluated. From Fig. 7, it can be seen that the partial nitrification to nitrite was seriously affected due to the decreasing metabolic activities of AOB when the temperature decreased gradually

from 30°C to 15°C start on 150 days. Fig. 8 shows the results of the combined change of temperature from 30°C to 15°C with an increasing DO concentration from 1.0 mg/L to 3.0 mg/L over 60 days. The results indicate that the disadvantageous effects by the temperature could be decreased by changing DO concentration

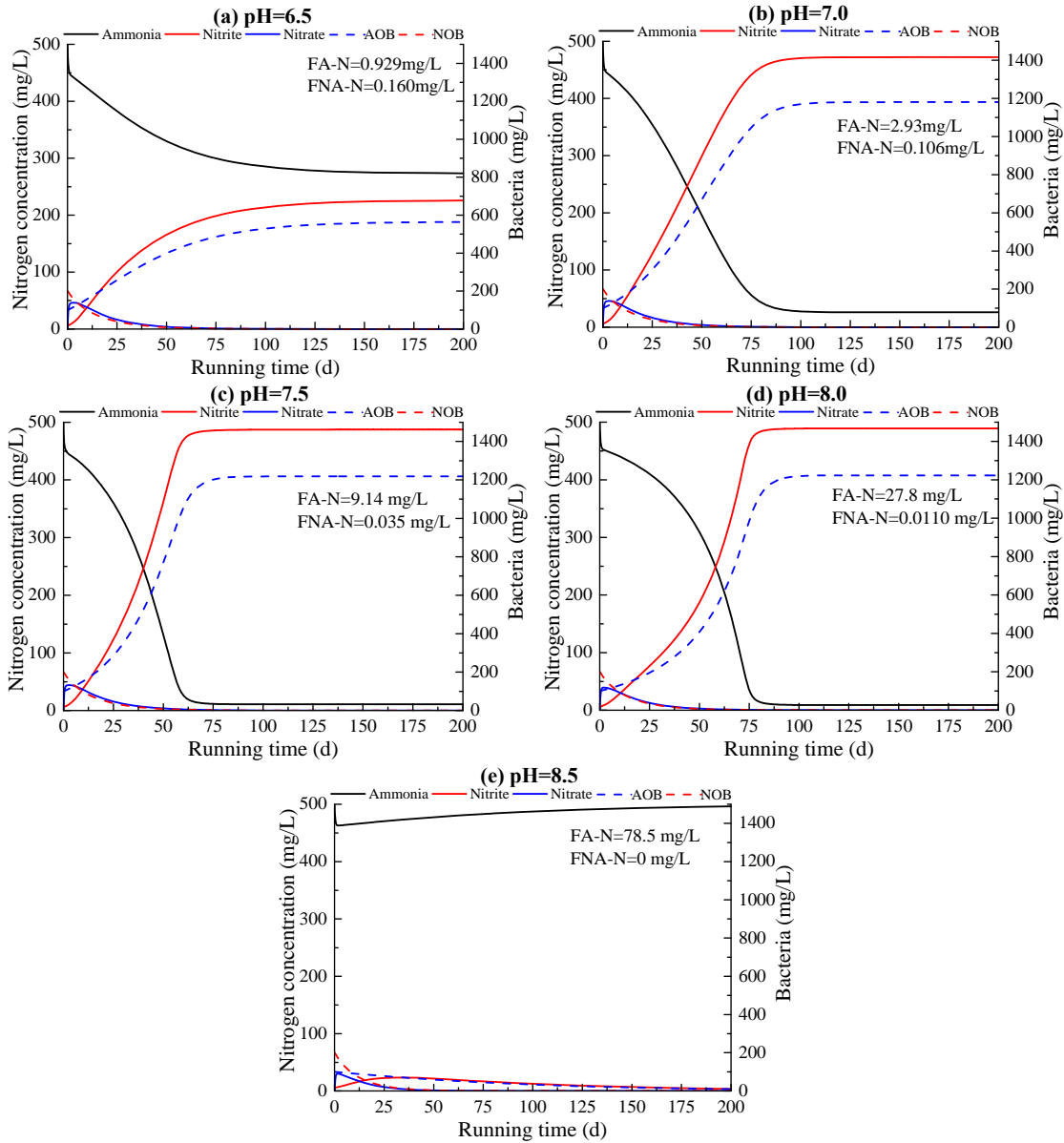


Figure 5 Effects of initial FA concentration on the nitrification under the conditions of $T = 25^{\circ}\text{C}$, initial $\text{NH}_4^+\text{-N} = 500 \text{ mg/L}$ and $\text{SRT} = 20 \text{ d}$ and $\text{DO} = 0.1 \text{ mg/L}$

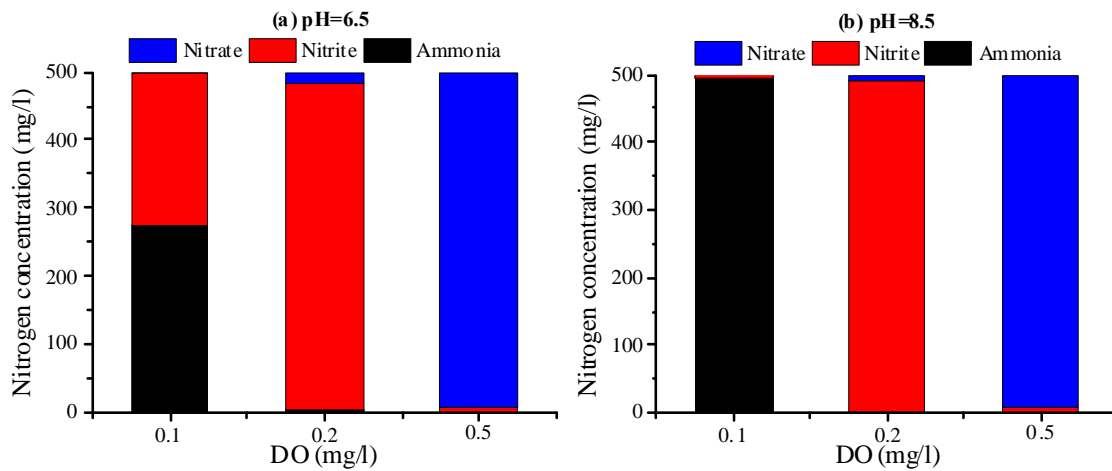


Figure 6 Steady state results of effects of DO concentration on nitrification process under the conditions of $T = 25^{\circ}\text{C}$, initial $\text{NH}_4^+\text{-N} = 500 \text{ mg/L}$ and $\text{SRT} = 20 \text{ d}$: (a) FA-N concentration is lower than 1 mg/L ; FNA-N is 0.16 mg/L ($\text{DO} = 0.1 \text{ mg/L}$) and 0.338 mg/L ($\text{DO} = 0.2 \text{ mg/L}$); (b) FA-N concentration of 78.35 mg/L ; FNA-N is lower than 0.01 mg/L

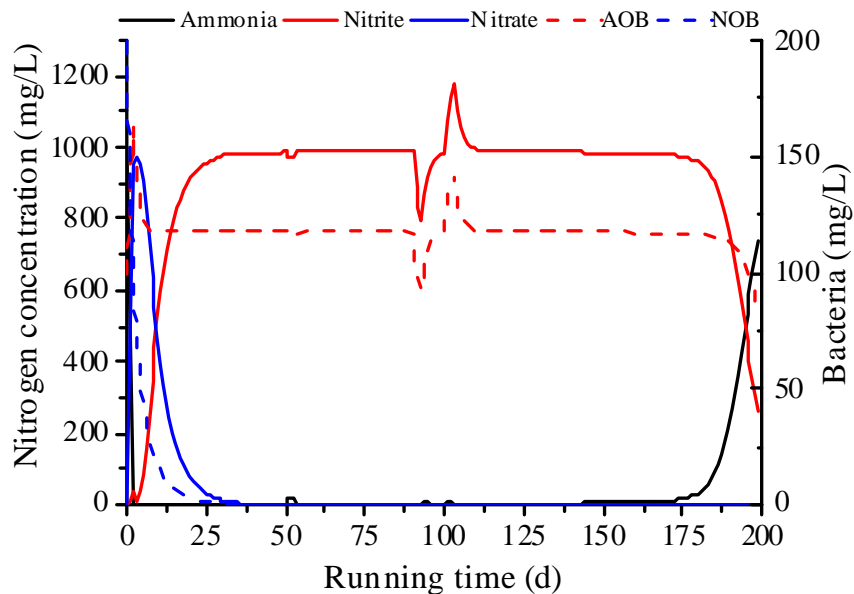


Figure 7 Long term stability of partial nitrification to variation of different operational parameters at the initial conditions of $\text{pH} = 8.0$, $T = 30^{\circ}\text{C}$, initial $\text{NH}_3\text{-N} = 1000 \text{ mg/L}$, $\text{DO} = 1.0 \text{ mg/L}$ and $\text{SRT} = 2 \text{ d}$. On 50 days, DO concentration changed from 1.0 mg/L to 0.5 mg/L for 3 days and then on 60 days, DO concentration changed from 1.0 mg/L to 1.5 mg/L for 3 days; the variation of pH value of ± 0.5 happens on 70 days and 80 days; on 90 day, the influent ammonia concentration decreased 250 mg/L for 3 days and then on 100 day, ammonia concentration increased 250 mg/L for 3 days; the temperature started to decrease gradually from 30°C on 150 days to 15°C on 200 days

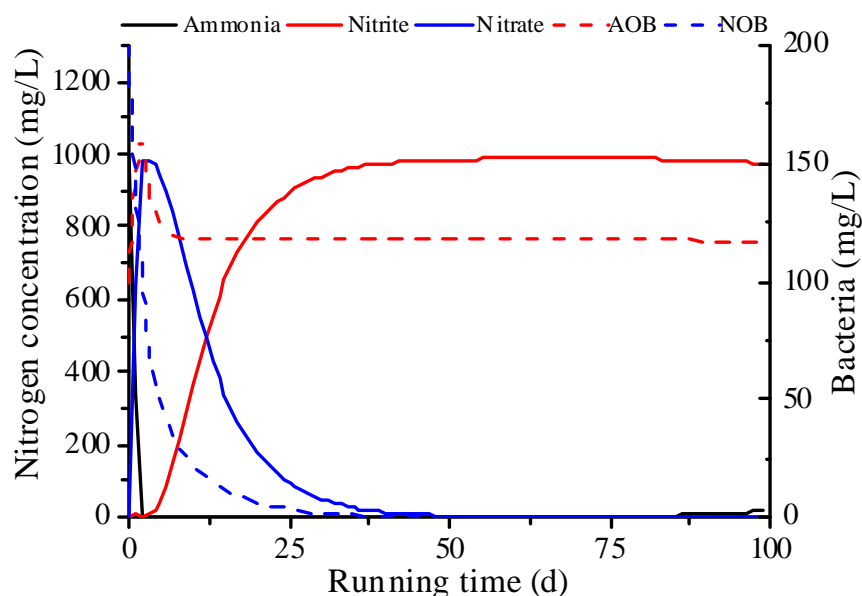


Figure 8 Long term stability of partial nitrification to variation of temperature combined with the change of DO concentration (temperature from 30°C to 15°C with an increasing DO concentration from 1.0 mg/L to 3.0 mg/L) at the initial conditions of pH = 8.0, T = 30°C, initial NH₃-N = 1000 mg/L and SRT = 2 d

CONCLUSIONS

The effects of different operational parameters on the partial nitrification process were evaluated by mathematical model. We found that DO can be used as an independent control parameter to achieve the partial nitrification process, but it was shown that it must be accurately controlled because a small variation in DO is capable of destroying the process. The control of lower SRT is an efficient way to enrich AOB and wash out NOB, and it also can decrease the sensitivity of nitrification process to variation of DO. Higher temperature has the advantage of improving the metabolic activities of AOB, but low temperature can also be achieved by suitably increasing DO concentration. Neither FA nor FNA has any decisive effect on the accumulation of nitrite as long as they are in the range suggested in the literature.

The successful start-up partial nitrification process was shown to be remarkably stable

when subjected to variations of different parameters such as DO and pH and ammonia concentration. While seasonal changes of temperature can affect partial nitrification, it is due to ammonia accumulation as a result of the metabolic activities of AOB. It is suggested that increasing DO concentration make it possible to maintain system stability when confronted with seasonal changes of temperature.

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