Impact of influent ammonia concentration on partial nitrification of biological sand filter and kinetics

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Abstract. The impact of influent NH\textsubscript{4}+ concentration on partial nitrification performance was investigated in a biological sand filter. The removal kinetics model of NH\textsubscript{4}+ in partial nitrification-sand filter was established and its accuracy was verified. The results showed that the NH\textsubscript{4}+ removal rates and NO\textsubscript{2}-N accumulation rates stabled at about 60% and 94% respectively and the effluent NO\textsubscript{2}-N/NH\textsubscript{4}+ ratios were 1.20~1.39 when the hydraulic load was 1.0 m/d and the influent NH\textsubscript{4}+ concentration was 45~50 mg/L, indicating that the sand filter had good partial nitrification effect, and the effluent quality basically met the theoretical influent demand of anaerobic ammonia oxidation. The kinetic model of NH\textsubscript{4}+ removal in sand filter could be described as \( S_{t}/S_{0} = \exp(-1.0033S_{0}^{-1.1337}t) \) when the influent NH\textsubscript{4}+ concentration was 10.2~61.3 mg/L. The model had high accuracy and could provide scientific guidance for effluent quality prediction and optimization design.

1. Introduction

Anaerobic ammonia oxidation (ANAMMOX), as a new biological nitrogen removal technology for wastewater, has attracted much attention in the field of wastewater denitrification because of its advantages of saving a large amount of oxygen consumption, no need to add organic carbon sources and low sludge yield [1-3]. The reaction matrix of ANAMMOX is NH\textsubscript{4}+-N and NO\textsubscript{2}-N. The theoretical influent NO\textsubscript{2}-N/NH\textsubscript{4}+-N ratio is 1.32:1 [4]. However, the NO\textsubscript{2}-N/NH\textsubscript{4}+-N ratio of actual wastewater is usually low, which can not meet the needs of ANAMMOX. Therefore, the removal rate of NH\textsubscript{4}+-N is about 60% by partial nitrification, and the concentration ratio of NO\textsubscript{2}-N to NH\textsubscript{4}+-N in effluent reaches or approaches 1.32, which is the precondition and key to realize ANAMMOX [5].

In recent years, scholars at home and abroad have achieved partial nitrification start-up [6-8] by regulating dissolved oxygen, hydraulic retention time and ammonia-nitrogen load, and investigated the effects of temperature, influent pH, matrix concentration and other factors on partial nitrification performance [9,10]. However, most of the studies focused on activated sludge systems. There are few studies on fixed-bed biofilm systems. Influent NH\textsubscript{4}+-N concentration is an important factor affecting partial nitrification. It is of great significance to study the migration and transformation of NH\textsubscript{4}+-N in the reaction system to analyze its influence mechanism on partial nitrification. Recently, more and more researches have been reported on the use of mathematical models to study the migration and
transformation of nitrogen pollutants [11]. The application of mathematical model provides an effective tool for the stable operation and optimal design of wastewater treatment process, but there are few reports on partial nitrification kinetics.

In view of this, this study selected a typical fixed-bed biofilm reactor - biological sand filter to treat simulated wastewater. On the basis of successful start-up of partial nitrification, the influence of influent \( \text{NH}_4^+ - \text{N} \) concentration on partial nitrification performance was investigated. At the same time, a partial nitrification kinetic model was constructed to determine the model parameters. It provides a scientific reference for water quality prediction and optimization design of partial nitrification.

2. Materials and Methods

2.1. Experimental device and operating conditions
The total height of the biological sand filter is 100 cm, the inner diameter is 7.04 cm, the height of filter material (made of natural river sand, shell sand and zeolite sand, volume ratio is 6:3:1, particle size is 0.5~1.0 mm) is 75 cm. The returned sludge from secondary sedimentation tank (MLSS is 7600 mg/L) is used as the inoculated sludge. 2.5 cm thick gravel layers are laid on the top and bottom of the filter respectively to cushion and support. The side wall of the filter material is provided with a water intake at intervals of 15 cm, numbering 1#~6# from top to bottom. The peristaltic pump is used to feed water, the flowmeter and relay are used to control the intake water volume and intake time respectively. It runs 2 cycles a day, 12 hours a cycle, wet-dry ratio 1:3, hydraulic load 1.0 m/d, and temperature 25±1 °C during the experiment.

2.2. Influent quality
Artificial simulated sewage was used in the experiment. The influent COD, \( \text{NO}_x^- - \text{N} \) and TP concentrations were 120~140, 0~0.5 and 2.5~4.2 mg/L respectively by adding \( \text{C}_6\text{H}_{12}\text{O}_6 \), \( \text{NaNO}_2 \), \( \text{KNO}_3 \) and \( \text{KH}_2\text{PO}_4 \) to tap water. The influent pH was 7.2~7.8 by adding 0.1 mol/L HCl and 0.1 mol/L NaOH, and alkalinity was supplemented by adding appropriate NaHCO\(_3\). The concentration of influent \( \text{NH}_4^+ - \text{N} \) was adjusted by adding \( \text{NH}_4\text{Cl} \), and the specific concentration was adjusted according to the experimental requirements.

2.3. Experimental scheme
On the basis of successful start-up of partial nitrification in biological sand filter, the influent \( \text{NH}_4^+ - \text{N} \) concentration was adjusted to 10~15, 25~30, 45~50, 65~70, 95~100, 145~150 mg/L respectively. After each concentration condition ran for 10 cycles, water samples were taken at 75 cm height for detection. The effect of influent \( \text{NH}_4^+ - \text{N} \) concentration on partial nitrification performance of sand filter was investigated. Then, changing the concentration of \( \text{NH}_4^+ - \text{N} \) in the influent, investigating the characteristics of \( \text{NH}_4^+ - \text{N} \) transformation along the way, using origin 9.0 to fit the experimental results, determine the kinetic parameters of \( \text{NH}_4^+ - \text{N} \) removal, construct the dynamic model and verify the accuracy of the model.

2.4. Analysis items and methods

2.4.1. Water quality analysis. The test methods of \( \text{NH}_4^+ - \text{N} \), \( \text{NO}_2^- - \text{N} \) and \( \text{NO}_3^- - \text{N} \) referred to Water and Wastewater Monitoring and Analysis Methods (4th Edition, China). According to the influent \( \text{NH}_4^+ - \text{N} \) concentration (inf. \( \text{NH}_4^+ - \text{N} \)), effluent \( \text{NH}_4^+ - \text{N} \) concentration (eff. \( \text{NH}_4^+ - \text{N} \)), effluent \( \text{NO}_2^- - \text{N} \) concentration (eff. \( \text{NO}_2^- - \text{N} \)), effluent \( \text{NO}_3^- - \text{N} \) concentration (eff. \( \text{NO}_3^- - \text{N} \)), the \( \text{NH}_4^+ - \text{N} \) removal rate (ARR), \( \text{NO}_2^- - \text{N} \) accumulation rate (NAR), effluent \( \text{NO}_2^- - \text{N} / \text{NH}_4^+ - \text{N} \) concentration ratio (NNR) were calculated by formula (1) ~ (3).

\[
\text{ARR} \times 100\% = \frac{\text{inf.} \ \text{NH}_4^+ - \text{N} - \text{eff.} \ \text{NH}_4^+ - \text{N}}{\text{inf.} \ \text{NH}_4^+ - \text{N}} \times 100\% \quad (1)
\]
2.4.2. Kinetic model. The biological sand filter can be considered as a push-flow reactor, which consists of countless fully mixed reactors connected in series by continuous flow. In the process of removing pollutants by microorganisms, the zero-order reaction is the main reaction when the concentration of matrix is relatively high, and the first-order reaction is the main reaction when the concentration of matrix is relatively low [12]. Hence, the removal rule of NH$_4^+$-N by biological sand filter during stable operation in this study conforms to the first-order reaction:

\[
\ln\left(\frac{S_0}{S_h}\right) = -mh
\]  

Where \( h \) denotes the effluent height, cm; \( S_0 \) denotes inf. NH$_4^+$-N, mg/L; \( S_h \) denotes eff. NH$_4^+$-N at the height of \( h \), mg/L; \( m \) denotes the removal rate constant of NH$_4^+$-N. When the structure, material properties, biofilm properties and environmental conditions of the biological sand filter are fixed, the \( m \) value is closely related to \( S_0 \) and hydraulic load (\( q \)). It can be expressed as formula (5):

\[
m = kS_0^\alpha q^\beta
\]

Where \( k \) denotes the coefficients related to \( S_0 \) and \( q \), \( \alpha \) denotes the coefficients related to \( S_0 \), and \( \beta \) denotes the coefficients related to \( q \). The kinetics equation of NH$_4^+$-N removal can be expressed as formula (6):

\[
S_h/S_0 = e^{-ks_0^\alpha q^\beta h}
\]

3. Results and Discussion

3.1. Impact of influent NH$_4^+$-N concentration

Fig. 1 shows the change of nitrogen pollutants in the effluent of sand filter under different influent NH$_4^+$-N concentration. When the influent NH$_4^+$-N concentration was 45~50 mg/L, the ARR and NAR remained about 60% and 94% respectively. The NNR in effluent was 1.20~1.39. The partial nitrification performance of sand filter was good, and the effluent water quality basically met the theoretical requirement of ANAMMOX.

When the influent NH$_4^+$-N concentration was lower than 45~50 mg/L, the adsorption sites and dissolved oxygen content in the filter were abundant due to the decrease of the total amount of NH$_4^+$-N in influent, and the removal rate of NH$_4^+$-N increased. When the influent NH$_4^+$-N concentration was 10~15 mg/L, NH$_4^+$-N was converted to NO$_2^-$-N in large quantities, and then further converted to NO$_3^-$-N. The NAR decreased to about 40%. Because the concentration of NH$_4^+$-N in effluent was very low, the NNR in effluent was much higher than the theoretical value of ANAMMOX. When the influent NH$_4^+$-N concentration was higher than 45~50 mg/L, although the NAR remained above 90%, the ARR decreased. The high concentration of NH$_4^+$-N in effluent led to the lower NNR ratios in effluent, which can not meet the influent requirement of ANAMMOX.
3.2. Kinetics of partial nitrification

The effluent NH$_4^+$-N concentration ($S_h$) corresponding to different effluent height ($h$) under different influent NH$_4^+$-N concentration ($S_0$) is shown in Table 1. Formula (4) is used to fit the relationship between $h$ and $S_h/S_0$. The fitting curves and parameters are shown in Figure 2(a).

### Table 1. Variation of eff. NH$_4^+$-N along the path.

| Test No. | 0 cm | 15 cm | 30 cm | 45 cm | 60 cm | 75 cm |
|----------|------|-------|-------|-------|-------|-------|
| T1       | 61.3 | 52.4  | 46.3  | 41.6  | 38.9  | 35.7  |
| T2       | 47.6 | 40.1  | 32.8  | 25.6  | 21.7  | 18.9  |
| T3       | 37.5 | 27.4  | 20.5  | 15.3  | 13.1  | 11.4  |
| T4       | 28.6 | 20.7  | 13.6  | 8.7   | 6.4   | 3.9   |
| T5       | 19.4 | 13.1  | 7.9   | 4.2   | 2.9   | 1.7   |
| T6       | 10.2 | 3.1   | 1.3   | 0.8   | 0.5   | 0.4   |

According to the fitting results, the higher the concentration of NH$_4^+$-N in influent, the slower the $S_h/S_0$ decline rate with the height of filter material, the smaller the corresponding $m$ value, the slower the removal rate of NH$_4^+$-N. When the influent NH$_4^+$-N concentration was 47.6 mg/L, the ARR at the effluent height of 75 cm was 60.3%. When the influent NH$_4^+$-N concentration was 61.3 mg/L, the ARR at the effluent height of 75 cm was only 41.8%. It can be seen that the existing sand filter height was not enough to complete partial nitrification when the concentration of NH$_4^+$-N in the influent was too high. When the influent NH$_4^+$-N concentration was 10.2, 19.4, 28.6 and 37.5 mg/L, the ARRs reached 60% at the height of 0~15, 30~45, 30~45 and 45~60 cm, respectively. The lower the influent NH$_4^+$-N
concentration, the lower the sand filter height required to achieve the same NH$_4^+$-N removal rate. The
determination coefficients $R^2$ of the fitting curves were higher than 0.96, which indicated that the
removal process of NH$_4^+$-N followed the first-order reaction kinetics.

**Fig. 2** Fitting curves of (a) $S_h/S_0$ variation with $h$, (b) $S_0$ variation with $m$.

Figure 2 (b) shows the relationship between $S_0$ and $m$ when $q$ was fixed at 1.0 m/d. The relationship
between $S_0$ and $m$ can be expressed as follows:

$$m = 1.0033S_{0}^{-1.1337}$$  \(7\)

Formula (7) shows that $m$ was negatively correlated with $S_{0}$, that is, the higher the concentration of
NH$_4^+$-N in influent, the lower the NH$_4^+$-N removal rate constant. By substituting formula (7) for formula
(6), the removal kinetics model of NH$_4^+$-N in partial nitrification-biological sand filter was obtained as
follows:

$$\frac{S_h}{S_0} = e^{-1.0033S_{0}^{-1.1337}h}$$  \(8\)

### 3.3. Accuracy verification of kinetic model

To verify the accuracy of the kinetic model, the influent NH$_4^+$-N concentrations were changed to 60.2,
50.3, 40.4, 32.4, 21.6 and 15.2 mg/L, respectively, corresponding to the test numbers T7~T12. The measured NH$_4^+$-N concentration ($S_{he}$) of effluent along the path was compared with the calculated value ($S_{he}$) obtained by using model equation (8). The results are shown in Fig. 3.

**Fig. 3** The $S_{he}$ and $S_{ht}$ values of eff NH$_4^+$-N along the path.
As seen, $S_{he}$ and $S_{sh}$ had high coincidence with each other, and the average relative error was less than 10%. It showed that the kinetic model of NH$_4^+$-N removal had high accuracy.

4. Conclusion
When the hydraulic load was 1.0 m/d, the influent NH$_4^+$-N concentration was 45–50 mg/L and the effluent height was 75 cm, the removal rate of NH$_4^+$-N and the accumulation rate of NO$_2^-$-N in the biological sand filter are about 60% and 94% respectively, and the NO$_2^-$-N/NH$_4^+$-N in the effluent was 1.20–1.39, showing good partial nitrification effect. The effluent water quality can basically reach the influent requirements for ANAMMOX. When the influent NH$_4^+$-N concentration was 10.2–61.3 mg/L, the kinetic model of NH$_4^+$-N removal could be expressed as $S_t/S_0=\exp(-1.0033S_0^{-1.1337}h)$.

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References
[1] Wang Z, Peng Y, Lei M, et al. Continuous-flow combined process of nitritation and ANAMMOX for treatment of landfill leachate[J]. Bioresource Technology, 2016, 214:514-519.
[2] Laureni M, Falás P, Robin O, et al. Mainstream partial nitritation and anammox: long-term process stability and effluent quality at low temperatures[J]. Water Research, 2016, 101:628-639.
[3] Tang C J, Duan C S, Yu C, et al. Removal of nitrogen from wastewaters by anaerobic ammonium oxidation (ANAMMOX) using granules in upflow reactors[J]. Environmental Chemistry Letters, 2017, 15(2):1-18.
[4] Zheng D. Ammonium nitrogen removal from anaerobically digested effluent of swine wastewater using local sand[J]. Water Practice & Technology, 2011, 6(1):1-2.
[5] Huang X, Urata K, Wei Q, et al. Fast start-up of partial nitritation as pre-treatment for anammox in membrane bioreactor[J]. Biochemical Engineering Journal, 2016, 105:371-378.
[6] Chen Z, Wang X, Yang Y Y, et al. Partial nitrification and denitrification of mature landfill leachate using a pilot-scale continuous activated sludge process at low dissolved oxygen[J]. Bioresource Technology, 2016, 218:580-588.
[7] Soliman M, Eldyasti A. Development of partial nitrification as a first step of nitrite shunt process in a Sequential Batch Reactor (SBR) using Ammonium Oxidizing Bacteria (AOB) controlled by mixing regime[J]. Bioresource Technology, 2016, 221:85-95.
[8] Wang L, Zheng P, Abbas G, et al. A start-up strategy for high-rate partial nitritation based on DO-HRT control[J]. Process Biochemistry, 2016, 51(1):95-104.
[9] Tomaszewski M, Cema G, Ziembińska-Buczyńska A. Influence of temperature and pH on the anammox process: a review and meta-analysis[J]. Chemosphere, 2017, 182:203-214.
[10] Yang W, He S, Han M, et al. Nitrogen removal performance and microbial community structure in the start-up and substrate inhibition stages of an anammox reactor[J]. Journal of Bioscience & Bioengineering, 2018, 126(1):88-95.
[11] Abbas G, Wang L, Li W, et al. Kinetics of nitrogen removal in pilot-scale internal-loop airlift bio-particle reactor for simultaneous partial nitrification and anaerobic ammonia oxidation[J]. Ecological Engineering, 2015, 74:356-363.
[12] Mann A T, Stephenson T. Modelling biological aerated filters for wastewater treatment[J]. Water Research, 1996, 31(10):2443-2448.