Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1053531

57 (2016) 12763–12769
June

Taylor & Francis
Taylor & Francis Group

Research on the large-scale application of nitrogen removal for the treatment of synthetic ammonia wastewater

Yufei Bao*, Meng Li, Qian Zhang

School of Civil Engineering and Architecture, Wuhan University of Technology, Wuhan 430070, P.R. China, Tel. +86 18986102232; emails: 781864436@qq.com (Y. Bao), Limeng189@126.com (M. Li), qianzhang@whut.edu.cn (Q. Zhang)

Received 15 October 2014; Accepted 15 May 2015

ABSTRACT

The capability of anoxic–aerobic (A/O) process treatment and influencing factors of high concentration ammonia industrial wastewater were studied in this paper. Results showed that the A/O process system had achieved favorable performance and the quality of effluent could meet the direct emission standard of *Discharge standard of water pollutants for ammonia industry* (GB13458-2013) under the optimal conditions as follows: the perfect inflow loading of ammonia 0.12 kg/(m^3 d), the mixed liquid recycle ratio (*R*) 200%, and sludge return ratio 80%, the carbon-to-nitrogen ratio (C/N ratio) 4.5–5.5. Besides, the results also confirmed that the activity of nitrifying bacteria in activated sludge was greatly inhibited due to the high concentration of free ammonia (FA). In addition, carbon shortage had a marked effect on the denitrification efficiency of the system.

Keywords: High-content ammonia nitrogen; Synthetic ammonia wastewater; Nitrogen removal; C/N ratio; Ammonia loading

1. Introduction

The pollution of synthetic ammonia wastewater has been a serious environmental and public concern worldwide because it contains important nutrient that can cause water eutrophication and ecological environment contamination [1,2]. It is also well known that biological nitrification–denitrification is the most commonly used process for nitrogen removal of wastewater [3]. Nitrification is an aerobic–autotrophic process used for conversion of ammonia to nitrate. Ammonia is transformed into nitrite by *Nitrosomonas* species in the first stage and nitrite is converted to nitrate by *Nitrobacter* species in the second. Denitrification is an anoxic–heterotrophic process used for conversion of nitrate to nitrogen gas by denitrifying organisms. These two processes are usually realized in two separate units since each process requires different environmental conditions.

Numerous studies were reported in literature for nitrification and denitrification of wastewater. The lab-scale researched carbon-to-nitrogen ratio (C/N) ratio required for nearly complete denitrification (98–100%) was 0.9–6.0 according to different carbon sources and $[NO_2^- - N]/[NO_x^- - N]$ ratios [4,5]. However, the C/N ratio must be properly controlled. Over addition of carbon (such as methanol or benzoic acid) would seriously inhibit the activity of denitrifying sludge [6]. Inhibition by FA was observed by many researchers [7–9]. They realized that inhibitory concentration of FA was indentified ranging from 0.1 to 150 mg/L. But the inhibition was

*Corresponding author.

not permanent and could be relieved by adjusting operational conditions. Denitrifying organisms could tolerate pH between 6 and 9 and the optimal pH was reported as pH 7–8 [10,11]. The MBR process was conducted that denitrification was limited by the availability of chemical oxygen demand (COD_{cr}) in the influent wastewater when operating at an *R* of three and higher [12,13]. This resulted in a deterioration of total nitrogen (TN) removal efficiency when operating at a higher *R* [14].

Systematic studies investigated effects of important influencing factors on the performance of nitrification–denitrification process while lacking practical research of large-scale studies [15]. For this reason, the influences of pH, C/N ratio, mixed liquid recycle ratio (*R*), and other running conditions on high-content ammonia nitrogen and nitrite wastewater of large-scale practical engineering were investigated to get a better understanding of the rules of biological nitrogen removal and mechanisms of microbial activities. Additionally, influences of the ammonia nitrogen loading and concentration of FA were also discussed in this paper. Therefore, the conclusions are of high significance for practical treatment of high-content ammonia nitrogen and nitrite wastewater.

2. Materials and methods

2.1. Characteristics of industrial wastewater

The synthetic ammonia wastewater is originated from a chemical fertilizer plant, which is located in Yichang, Central China. The raw influent and the national standard of effluent quality are characterized in Table 1.

From Table 1, it could be noted that the concentration of NH_4^+-N was more than 250 mg/L and TN was greater than 300 mg/L. Moreover, the C/N ratio of influent was found to be 1.5–2. It is the typical high-content ammonia nitrogen and low C/N ratio wastewater. According to the report of Water Pollution Control Federation, it was insufficient to complete the reaction of denitrification within the system, posing a great challenge to achieve an effective treatment.

2.2. System setup and operational produces

This process was designed with the wastewater treatment capacity of 300 m^3/h and the main treatment processes were depicted in Fig. 1. The system consisted of a column tower for stripping the free ammonia (FA) of wastewater. Then, an anoxic–aerobic (A/O) process constructed of concretes was used as biological treatment system with a working volume of 3500 m^3 ($L \times B \times H = 50\ m \times 10\ m \times 7\ m$) of the anoxic tank and 6720 m^3 ($L \times B \times H = 80\ m \times 12\ m \times 7\ m$) of the aerobic tank. The internal mixed liquor flowed from the aerobic tank to the anoxic tank.

The start-up process went through about 95 d with the following four main steps.

First step: The stage of adding activated sludge (1–8 d). This system was seeded with sludge from municipal wastewater treatment plant with simultaneous nitrification and denitrification. The intermittent influent was adopted in order to allow bacteria to adjust to the raw water gradually.

Second step: The stage of cultivating activated sludge (9–36 d). Kept inflow of raw water up to the design flow little by little until the concentration of sludge reached 3500 mg/L and the sludge settling property was improved. At the same time, adding carbon source to anoxic tank was necessary for further cultivating denitrifying bacteria.

Third step: The stage of exploring the optimum operating parameter (37–65 d). In order to achieve the maximum nitrogen removal effect, each operating parameter was changed according to the feedback of daily observation and operational data.

Fourth step: Continuous stable operation stage (66–95 d). The system ran for another 30 d at the best conditions to observe the true and stable performance of this system.

2.3. Analytical methods

Mixed liquor samples were taken from the influent and effluent of anoxic and aerobic tanks every eight hours, respectively. pH, ammonia nitrogen (NH_4^+-N), TN, nitrate (NO_3^-), nitrite (NO_2^-), COD_{cr}, mixed liquor suspended solids (MLSS), dissolved oxygen (DO), and SV_{30} were analyzed three times a day with the standard methods (APHA,2005).

Table 1
Characteristics of raw influent and the standard of effluent quality (mg/L, except for pH)

Parameter	COD_{cr}	TN	NH_4^+-N	NO_3^--N	NO_2^--N	pH
Characteristics of raw influent	500–800	300–450	250–400	50–100	≤10	6.20–9.62
Standard of effluent quality	≤100	≤50	≤40			6–9

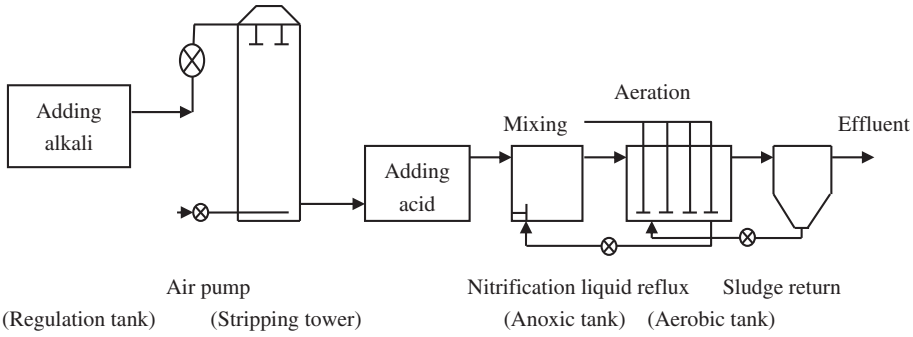

Fig. 1. Schematic diagram of large-scale experimental systems for treatment of synthetic ammonia wastewater.

Table 2
Parameters of A/O process

Parameters	
Inflow (m^3/h)	300
Mixed liquid recycle ratio (%)	50–400
Sludge return ratio (%)	50–100
DO (mg/L) (Anoxic tank)	0.2–0.5
DO (mg/L) (Aerobic tank)	2–4
SV_{30} (%)	30–50
MLSS (mg/L)	3,500–5,000

2.4. Operating parameters of the debugging process

The system operated 95 d and continuous flow was adopted from the ninth day with the temperature of 30–35°C. The operating parameters were followed in Table 2.

3. Results and discussion

3.1. Influence of pH

Before entering the A/O process, the industrial wastewater went through the stripping tower in the controlling pH value of 10–11 and the temperature of 30–35°C. So it was necessary to add acid (hydrochloric acid) to adjust the pH in the pH regulator. The pH value was set from 6.0 to 9.0 at the step of 0.5, and the system ran for five days stably at each pH value. The removal efficiencies of TN and NH_4^+-N changing with pH value were presented in Fig. 2. The other influence factors such as mixed liquid recycle ratio (R), C/N ratio, and ammonia loading were kept constant.

As was exhibited in Fig. 2, when pH value was lower than 6.4, the NH_4^+-N removal efficiency kept pretty low at 67.4% which reflected the inhibition of nitrification. When pH value increased from 6.4 to 7.0, the removal efficiency began to ascend sharply up to 92.1% owing to the biomass reactivation. However,

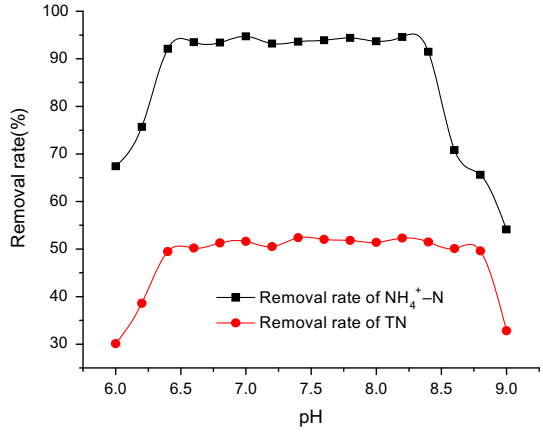

Fig. 2. Effect of pH value on the removal efficiencies of TN and NH_4^+-N (R = 200%, C/N ratio = 1.75 ± 0.25, ammonia loading = (0.11 ± 0.10) kg/(m^3 d)).

when pH value continued to rise to 8.4, it was of little effect on nitrification. When pH value exceeded 8.6, a clear inhibition of nitrification was found by the fact that the NH_4^+-N removal efficiency decreased to 70.8%. Besides, the TN removal efficiency reached about 50% and maintained stable. The changing rules of TN removal were similar to those of NH_4^+-N, but with a wider range of pH value up to 8.8.

These results showed that complete nitrification took effect in a wide range of pH value (between 6.4 and 8.4), since the nitrifying bacteria were adapted to more alkaline environment. Meanwhile, denitrification took place in a wider range of pH value (between 6.4 and 8.8) for alkalinity could be generated during the denitrification process. However, obvious inhibition of nitrification and denitrification was observed when pH value was lower than 6.4 and over 8.8. The reason was simple that too acidic or too alkaline environment reduced the microbial enzyme's activity and led to the partial decomposition of cells, resulting in the decrease in NH_4^+-N and TN removal efficiencies.

3.2. Influence of mixed liquid recycle ratio (R)

The influence of mixed liquid recycle ratio (*R*) on nitrification and denitrification efficiencies were studied when the activated sludge became mature and stable. The mixed recycle ratio was controlled by two variable frequency pumps, and was enhanced gradually from 50 to 350% at a step of 50%. Predictably, TN and NH_4^+–N removal efficiencies would fluctuate for the first couple of days, when each *R* was set. *R* would be increased as the removal efficiencies kept relatively constant for five days. The average value of these five days' removal efficiencies would indicate the performance of this ratio. Changes of TN removal efficiency, NH_4^+–N removal efficiency, and concentrations of other nitrogen with different *R* were reflected in Figs. 3 and 4, respectively.

As was exhibited in Fig. 3, when *R* increased from 50 to 350%, the nitrification process had been fully accomplished with enough aeration time, which could be confirmed that little nitrite accumulation was found and nitrate concentration increased from 143 to 232 mg/L. As a result, the denitrification efficiency would be greatly improved from 35 to 61%. What's more, the TN removal performance increased steeply at the beginning along with the increasing *R* and then became gentle, owing to the quantitative limitation of carbon source which could provide electron donor for the denitrifying bacteria.

From Fig. 4, it could be seen that the ammonia–nitrogen removal efficiency enhanced from 85 to 95.8% as *R* increased from 5 to 150%. The reasons were as follows: the raw water was diluted with recirculation water. As a result, ammonia loading decreased with the rise of *R*, leading to the enhancement of nitrification efficiency [12]. However, a further

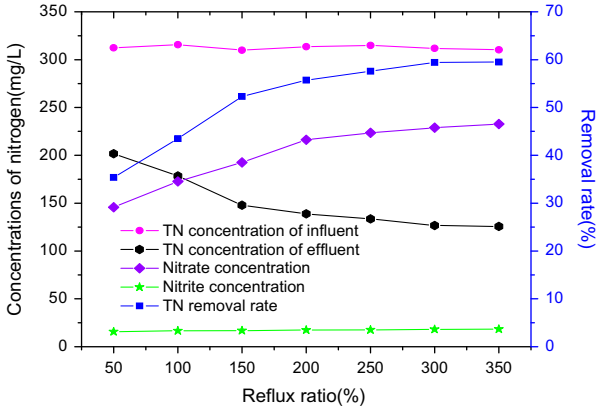

Fig. 3. Effect of *R* on TN removal efficiency and concentrations of other forms of nitrogen in anoxic tank (pH 7.5 ± 0.5, C/N ratio = 1.75 ± 0.25, ammonia loading = (0.11 ± 0.10) kg/(m^3 d)).

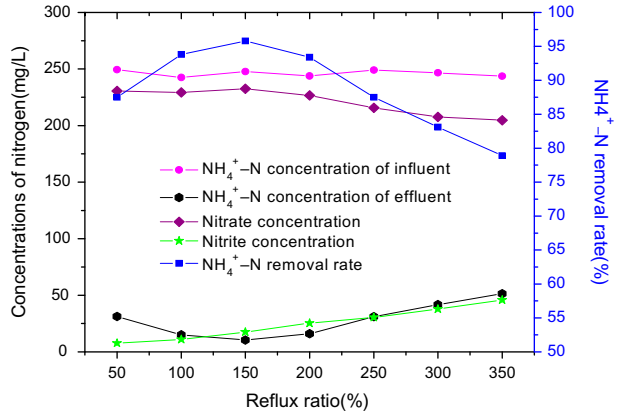

Fig. 4. Effect of *R* on NH_4^+–N removal efficiency and concentrations of other forms of nitrogen in aerobic tank (pH 7.5 ± 0.5, C/N ratio = 1.75 ± 0.25, ammonia loading = (0.11 ± 0.10) kg/(m^3 d)).

increase in *R* from 150 to 350% resulted in a corresponding deterioration in NH_4^+–N removal efficiency from 95.8 to 80.9%. The results could be explained that the every hydraulic residence time would become shorter with the increase in *R*, which inevitably took a turn for the worse resulting from heterogeneous biomass distribution and short flow phenomenon. Additionally, nitrite concentration would continue to rise when *R* increased (as shown in Fig. 4), which would be unfavorable to nitrification performance. So to sum up, *R* of 200% was taken according to the comprehensive analysis of TN and NH_4^+–N removal efficiency.

3.3. Performance of C/N ratio

It was found that the final TN removal efficiency only achieved about 60% and the quality of effluent could not meet the standard (GB13458-2013) during 24–36 d under the optimum operating parameters. According to the traditional nitrogen removal theory, 2.86 g COD_{cr} is a necessity for chemically denitrifying 1 g NO_3^-–N [16]. The actual required COD_{cr}; however, is greater than 2.86 g due to the requirement for cell growth. So the serious lack of carbon sources would lead to relatively poor denitrification performance. Therefore, it was essential to add external carbon sources (methanol etc.) to improve the C/N ratio. In the experiment, C/N ratio would be increased when the TN removal efficiency maintained stable for five days. Fig. 5 indicated the effect of C/N ratio on denitrification and other forms of nitrogen concentrations.

Fig. 5 illustrated that the C/N ratio in the anoxic tank had a notable impact on TN removal efficiency,

which increased from 45 to 85% when the C/N ratio changed from 1.5 to 5.5. Then, the quality of effluent fulfilled the direct emission requirements of GB13458-2013. In addition, it was found that the nitrate concentration stopped to decrease nearly at 220 mg/L when R was controlled of 200%. A possible biological explanation was listed below: in terms of denitrification mechanisms, it was reported that the expression of nitrate reductate periplasmic Nar was not dependent on the concentration of nitrates but affected by carbon sources [17]. What's more, reducing coenzyme was positively correlated to nitrate concentration only with abundant carbon sources [18]. Therefore, it could be deluded that the denitrification efficiency was subject to the insufficiency of carbon and kept low even under relatively high nitrate concentration, which might have been conductive to denification process by providing more electron acceptors.

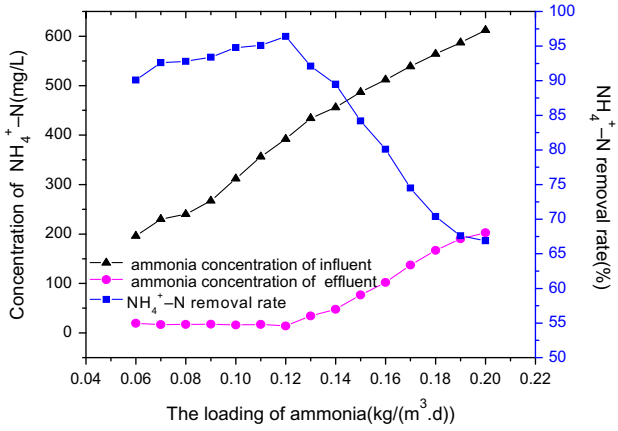

Fig. 6. Effect of the loading of NH_4^+-N on the removal efficiency of NH_4^+-N (pH 7.5 ± 0.5, R = 200%, C/N ratio = 5.0 ± 0.5).

3.4. Influence of the ammonia nitrogen loading

The concentration of influent ammonia nitrogen increased gradually as the process went on. Fig. 6 showed the variation of NH_4^+-N removal efficiency with the changes of ammonia nitrogen loading.

As was depicted in Fig. 6, NH_4^+-N removal efficiency increased from 90.1 to 96.4%, when the ammonia loading of influent increased from 0.06 to 0.12 kg/(m^3 d). But when the loading of ammonia continued to increase and concentration of ammonia reached up to 392 mg/L, the removal efficiency of ammonia nitrogen decreased suddenly and ammonia concentration of effluent also reached up to 181 mg/L. Previous experiments showed that when the concentration of ammonia was lower than 392 mg/L, higher content ammonia would stimulate the growth of filamentous bacteria and enhance the density of *Zoogloea*. However, excessive growth of filamentous bacteria would bring about sludge bulking and biomass reduction. What's worse, it was found that high concentration of FA would affect the growth of nitrifying bacteria dramatically [19].

The ammonia nitrogen exists in water in two forms of NH_4^+ and FA (NH_3). The relationship between them is as follow:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (1)$$

Then, the water and ammonia ionization constants are substituted in the above dissociation equilibrium

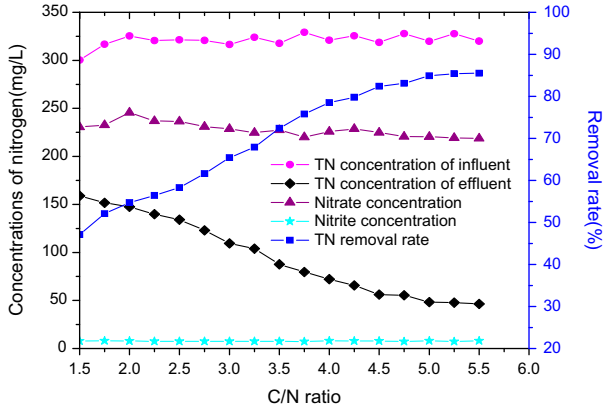

Fig. 5. Effect of C/N ratio on the removal efficiency of TN (pH 7.5 ± 0.5, R = 200%, ammonia loading = (0.11 ± 0.10) kg/(m^3 d)).

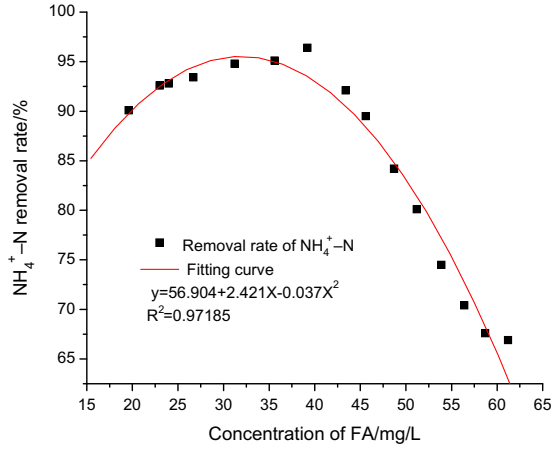

Fig. 7. The relationship between removal efficiency of NH_4^+-N and the concentration of FA.

Table 3
Summary of the effect of this system

Parameter		1–8 d	9–23 d	24–36 d	37–65 d	66–95 d
COD_{cr}	Influent (mg/L)	243.5	352.8	478.3	656.9	635.4
	Effluent (mg/L)	65.9	68.9	66.4	62.4	53.1
	Removal efficiency (%)	72.9	80.1	86.2	90.5	91.6
NH_4^+-N	Influent (mg/L)	135.4	155.7	217.6	275.2	268.9
	Effluent (mg/L)	47.3	30.8	15.3	13.6	9.0
	Removal efficiency (%)	65.1	80.2	93.0	95.1	96.7
TN	Influent (mg/L)	157.4	187.5	249.7	316.5	314.1
	Effluent (mg/L)	124.6	127.7	98.3	49.3	43.1
	Removal efficiency (%)	20.8	31.9	60.6	84.4	86.3

formula (1) so that the calculation formula for the FA is achieved.

$$C(\mathrm{FA}) = \frac{17}{14} \times \frac{C(\mathrm{NH_4^+}) \times 10^{\mathrm{pH}}}{\exp[6,334/(273+t)] + 10^{\mathrm{pH}}} \quad (2)$$

where C(FA) is the concentration of FA, mg/L; C (NH_4^+) represents the concentration of ammonia nitrogen, mg/L; t represents temperature, ℃. Chemically, it is well known that the concentration of FA increases as pH and temperature increase. FA concentration accounts for about 10% of the ammonia nitrogen concentration when pH 8 and $t = 30$℃. Fig. 7 reflected the relationship between removal efficiency of NH_4^+-N and the concentration of FA which was corresponding to the ammonia concentration of influent in Fig. 6.

Fig. 7 had shown a quadratic functional relationship between NH_4^+-N removal efficiency and FA concentration on the condition of ammonia loading ranging from 0.06 to 0.20 kg/(m^3 d). FA was beneficial to the nitrification when FA concentration was lower than 39.2 mg/L, while NH_4^+-N removal efficiency decreased rapidly when FA concentration continued to increase. It could be inferred that FA of low concentration could exert a catalytic effect on nitrifying bacteria, whereas too much FA would have a negative impact on oxidoreductase or hinder the electron transfer of nitrifying bacteria and some related enzymes in the process of nitrification, which made nitrification efficiency comparatively poor.

4. Operation result

After running for 95 d, the main characterizes of influent, effluent, and the average removal efficiency value were shown in Table 3.

From Table 3, it was observed that COD_{cr}, NH_4^+-N and TN removal efficiencies increased progressively with the system and the effluent met the required standard of GB13458-2013 eventually. The optimum operated parameters were also achieved as the average ammonia nitrogen loading of inflow was 0.12 kg/(m^3 d), the mixed liquid recycle ratio and sludge return ratio were 200 and 80%, respectively and the favorable C/N ratio was between 4.5 and 5.5.

5. Conclusions

The A/O process for enhancing nitrogen removal in the treatment of synthetic industrial wastewater was evaluated. Based on the results of experimental tests, the following conclusions were drawn:

(1) The A/O system discussed in this essay was able to treat synthetic ammonia wastewater effectively. The quality of effluent could meet the direct emission standard of *Discharge standard of water pollutants for ammonia industry* (GB13458-2013).
(2) Over a wide range of pH (6.4–8.4), it was possible to achieve high nitrification and denitrification efficiency. With R increased in a certain range, the nitrification performance increased firstly and then decreased, while the denitrification efficiency enhanced gradually. The optimum R was 200%.
(3) Without external carbon source, the denitrification efficiency of the A/O system could only achieve 60% for the low C/N ratio (between 1.5 and 2) and hard to be further improved. When regulating the C/N ratio at 4.5–5.5 with methanol as external carbon source, the denitrification efficiency could be stabilized at about 85%.
(4) Nitrification efficiency would decrease rapidly when the loading ammonia was greater than 0.12 kg/(m^3 d). A quadratic functional relationship existed between NH_4^+-N removal efficiency and FA concentration with the optimum concentration of FA was 39.2 mg/L.

Acknowledgments

This work was financially supported by the National Nature Science Foundation of China (NSFC) (No. 51208397), the Fundamental Research Funds for the Central Universities (2013-IV-055), and Independent Innovation Fund for Wuhan University of Technology (No. 145206011).

References

[1] F.F. Wang, Y.H. Ding, L. Ge, H.Q. Ren, L.L. Ding, Effect of high-strength ammonia nitrogen acclimation on sludge activity in sequencing batch reactor, J. Environ. Sci. 22 (2010) 1683–1688.
[2] L. Michaud, J.P. Blancheton, V. Bruni, R. Piedrahita, Effect of particulate organic carbon on heterotrophic bacterial populations and nitrification efficiency in biological filters, Aquacult. Eng. 34(3) (2006) 224–233.
[3] H.M. Huang, J. Yang, D. Li, Recovery and removal of ammonia-nitrogen and phosphate from swine wastewater by internal recycling of struvite chlorination product, Bioresour. Technol. 172 (2014) 253–259.
[4] H.D. Ryu, D. Kim, H.E. Lim, S.L. Lee, Nitrogen removal from low carbon-to nitrogen wastewater in four-stage biological aerated filter system, Process Biochem. 43(7) (2008) 729–735.
[5] X.Y. Fan, H.Q. Li, P. Yang, B. Lai, Effect of C/N ratio and aeration rate on performance of internal cycle MBR with synthetic wastewater, Desalin. Water Treat. 54 (2015) 573–580.
[6] L. Lin, S.H. Yuan, J. Chen, Z.Q. Xu, X.H. Lu, Removal of ammonia nitrogen in wastewater by microwave radiation, J. Hazard. Mater. 161 (2009) 1063–1068.
[7] Y. Liu, P. Maite, Z.G. Yuan, The effect of free nitrous acid on the anabolic and catabolic processes of glycogen accumulating organisms, Water Res. 44(9) (2010) 2901–2909.
[8] M. Pijuan, L. Ye, Z. Yuan, Free nitrous acid inhibition on the aerobic metabolism of poly-phosphate accumulating organisms, Water Res. 44(20) (2010) 6063–6072.
[9] X.L. Zheng, P. Sun, J.Q. Lou, J. Cai, Y.Q. Song, S.J. Yu, X.Y. Lu, Inhibition of free ammonia to the granule-based enhanced biological phosphorus removal system and the recoverability, Bioresour. Technol. 148 (2013) 343–351.
[10] G. Ruiz, D. Jeison, R. Chamy, Nitrification with high nitrite accumulation for the treatment of wastewater with high ammonia concentration, Water Res. 37(6) (2002) 1371–1377.
[11] S. Lee, S. Maken, J.H. Jang, K. Park, J.W. Park, Development of physicochemical nitrogen removal process for high strength industrial wastewater, Water Res. 40(5) (2006) 975–980.
[12] T.W. Tan, H.Y. Ng, Influence of mixed liquor recycle ratio and dissolved oxygen on performance of pre-denitrification submerged membrane bioreactors, Water Res. 42(4–5) (2007) 1122–1132.
[13] W.T. Mook, M.T. Chakrabarti, M.K. Aroua, G.M.A. Khan, B.S. Ali, M.S. Islam, M.A. Abu Hassan, Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture wastewater using electrochemical technology: A review, Desalination 285(31) (2012) 1–13.
[14] G. Ruiz, D. Jeison, O. Rubilar, G. Ciudad, R. Chamy, Nitrification-denitrification via nitrite accumulation for nitrogen removal from wastewater, Bioresour. Technol. 97(2) (2005) 330–335.
[15] A. Talaiekhozani, S. Jorfi, M.A. Fulazzaky, M. Ponraj, M.Z. Abd Majid, A.H. Navarchian, M.R. Talaie, S. Zare, Lab-scale optimization of propylene glycol removal from synthetic wastewater using activated sludge reactor, Desalin. Water Treat. 52 (2014) 3585–3593.
[16] S. Akizuki, K. Izumi, N. Nagao, T. Shiotani, C. Niwa, T. Toda, Effect of COD/NO_3-N ratio and seed sludge on simultaneous methanogenesis and denitrification in intermittent organic solid waste treatment, Int. Biodeterior. Biodegrad. 84 (2013) 8–13.
[17] K. Bernat, I. Wojnowska-Baryła, Carbon source in aerobic denitrification, Biochem. Eng. J. 36(2) (2007) 116–122.
[18] Y. Xue, F.L. Yang, S.T. Liu, Z.M. Fu, The influence of controlling factors on the start-up and operation for partial nitrification in membrane bioreactor, Bioresour. Technol. 100(3) (2009) 1055–1060.
[19] V.M. Vadivelu, J. Keller, Z. Yuan, Effect of free ammonia on the respiration and growth processes of an enriched Nitrobacter culture, Water Res. 41(4) (2007) 826–834.