Journal of Environmental Sciences Vol.17, No.5, pp.794—797, 2005

ISSN 1001-0742
CN11-2629/X

Article ID: 1001-0742(2005)05-0794-04 **CLC number**: X703; X17 **Document code**: A

Achieving and maintaining biological nitrogen removal via nitrite under normal conditions

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Abstract: The principal aim of this paper is to develop an approach to realize stable biological nitrogen removal via nitrite under normal conditions. Validation of the new method was established on laboratory-scale experiments applying the sequencing batch reactor(SBR) activated sludge process to domestic wastewater with low C/N ratio. The addition of sodium chloride(NaCl) to influent was established to achieve nitrite build-up. The high nitrite accumulation, depending on the salinity in influent and the application duration of salt, was obtained in SBRs treating saline wastewater. The maintenance results indicated that the real-time SBRs can maintain stable nitrite accumulation, but conversion from shorter nitrification-denitrification to full nitrification-denitrification was observed after some operation cycles in the other SBR with fixed-time control. The presented method is valuable to offer a solution to realize and to maintain nitrogen removal via nitrite under normal conditions.

Keywords: nitrite accumulation; salt selective inhibition; real-time control of nitrification; biological nitrogen removal via nitrite; nitrite-oxidizers; ammonium-oxidizers

Introduction

Nitrogen removal from wastewater has become an essential part of activated sludge processes as a result of the concern for eutrophication of the effluent receiving waters. Nitrification-denitrification via nitrite rather than nitrate is well established that it could save energy and shorten reaction time(Albeling, 1992). A number of factors can inhibit nitrite oxidizer, such as high free ammonia (FA) concentration (Villaverde, 2000), high temperature (Hellinga, 1998), high free hydroxylamine (FH) concentration, and low dissolved oxygen(DO) concentration (Helmer, 1999). Although these factors can obtain nitrite accumulation, high FA, high pH and high temperature are so special that they could not be found in common wastewater, and abnormal process condition such as low DO can result in sludge bulking and upset treatment performance. Moreover, more often due to the adaptation and the presence of *Nitrobacter*(Nguyen, 1992), maintaining biological nitrogen removal via nitrite become another problem. Until recently, achieving and holding nitrification at the intermediary level was not successful.

Of particular interest in achieving nitrite build-up is addition of chemical inhibitors or toxic substrate. Jooste and van Leeuwen(Jooste, 1993) observed that nitrite build-up in gold-mine service water was caused by the biotic oxidation of ammonia in presence of disinfectants such as chlorine, chlorine dioxide or bromine. The method can achieve nitrite accumulation under normal process conditions on base of the fact that nitrite-oxidizers can be selectively inhibited with the dosage of chemical inhibitors. In our previous investigations on biological treatment of saline wastewater, nitrite accumulation could also be found(Peng, 2004). That gives an extra new possibility that sodium chloride(NaCl) could be used as inhibitor to obtain nitrification/denitrification via nitrite. In comparison with disinfectants, NaCl, cheap commercial chemicals, has significant advantages, since it is easy to implement in wastewater treatment plants, especially in coastal cities where seawater offer a free resource for this kind of application. Owing to that, this work applied sodium chloride as inhibitor to domestic wastewater to achieve nitrogen removal via nitrite for the first time.

Maintaining strategy to deter growth of aerobic nitrite oxidizers, however, has to be applied after the majority of nitrite-oxidizers was washed out of treatment system and after stopping addition of inhibitors. In such system as ammonium-oxidizers predominates, one possible strategy in case nitrite-oxidizers outcompete ammonium-oxidizers is stopping aeration immediately after ammonia bas been completely oxidized. Some reports have suggested that for a nitrogen removal system, on-line measurements of oxidation-reduction potential (ORP), dissolved oxygen concentration(DO) and pH value contain some characteristic patterns that indicate the end of the biodegradation processes (Anthreottoia, 2001). Using these control parameters can offer a possibility of stopping the aeration just after completing removal of ammonia in SBR.

The specific aim of this work is to develop and evaluate the proposed approach to obtain and keep nitrogen removal bypassing nitrate under normal conditions.

1 Materials and methods

1.1 Reactor setup and operation

Biomass from an urban wastewater water treatment plant (WWTP) is seeded in the two lab-scale sequencing batch reactors(SBRs), which can be operated by fix-time cycling mode and real-time control mode(Fig.1). The SBRs worked in a temperature-controlled room at 18 to 22℃ with working volume of 10 L. SBR1 was operated with two 12 h cycles per day. Each cycle consisted 10 min fill, 6 h aerobic, 4 h anoxic, 1.5 h settling, and 20 min decant times. A fuzzy controller developed by our research group was applied in order to realize the fix-time cycling mode. The fuzzy controller uses pH as control parameter to change process phase due to the fact that the complete ammonia oxidation corresponded exactly to the valley in the pH versus time graphic. External carbon source(methanol) was added when

Foundation items: The Hi-Tech Research and Development Program(863) of China(2004AA601020); the National Natural Science Foundation of China(No. 50478047) and the Open Grant of Beijing Key Laboratory; * Corresponding author

anoxic phase began. Two reactors were operated in parallel with the same mixed liquor suspended solids (MLSS) at level of 2500—3000 mg/L. The effective SRT (sludge age), correcting for the aeration period and calculating on the basis of the aerobic sludge mass fraction, is about 18 d.

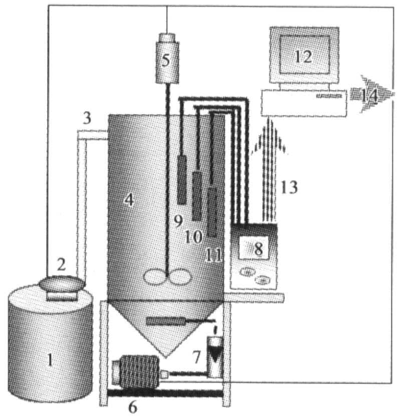

Fig.1 SBR diagram

1. feed tank; 2. lift pump; 3. feed pipe; 4. SBR reactor; 5. mixer; 6. air pump; 7. air flowmeter; 8. monitor; 9. DO probe; 10. pH probe; 11. ORP probe; 12. computer; 13. input cable; 14. output cable

1.2 Sewage and chemical inhibitors

The feed wastewater was collected from the sewer of Beijing University of Technology. The influent characteristics are listed in Table 1. Commercial NaCl was applied as the chemicals inhibitors. NaCl was added into storage tank to form saline sewage as SBR feed during achieving nitrite build-up. The salinity was adjusted according to experiment design.

Table 1 Influent characterization

Items	pH	COD, mg/L	BOD, mg/L	TN, mg/L	NH_4^+-N, mg/L
Range	7.2—7.7	190—325	102—183	51—95	32—85

1.3 Experimental design

With the aerobic-anoxic sequence, two parallel SBRs achieving complete nitrification-denitrification were dosed by certain concentration of NaCl to influent. The nitrite accumulation under conditions of different dosage of NaCl in influent and different application duration of salt was explored in experiments on achieving nitrite build-up. Optimum dosage and application duration of salt, which interact to determine the performance and stabilization of nitrite accumulation, was determined by the experiments. After accomplishing nitrite build-up, the salt addition was stopped and fresh sewage was applied in the two SBRs. According to different dosage and application duration of salt, the maintaining experiments in the two SBRs were conducted to establish validation of real-time control to hold the nitrification at the intermediary level.

1.4 Analytical methods

Samples withdraw from the liquid media during processing were centrifuged at 3000 r/min for 5 min to remove microorganism from liquid medium. Most routine chemical analyses (i.e. TN, NH_4^+-N, NO_3^--N, NO_2^--N, Cl^-) were conducted according to the standard methods (APHA, 1995).

2 Results and discussion

2.1 Nitrogen removal by nitrification and denitrification

Before adding salt into influent, the two SBRs achieved complete nitrification and denitrification. Fig.2 shows data from a typical cycle of nitrogen removal in SBR1 during steady states. With the ammonium degradation, there is a rapid increasing of nitrate and a slowly accumulation of nitrite. The removal efficiency of NH_4^+-N reached 100% after 3 h aeration. In 6 h aeration cycle, the other three hours contributed nothing to pollutants removal, but provided enough time for nitrite oxidation. When adding enough methanols as external carbon source in anoxic phase, nitrate nitrogen was removed linearly. The phenotype of nitrogen removal in two SBRs was established to be normal nitrification and denitrification. Fluctuations in influent ammonium concentration provided a useful tool to investigate whether ammonium concentration could change the type of nitrification. The ammonium concentration in the range of this waste contributed little to nitrification rate and nitrite accumulation ratio (data not shown).

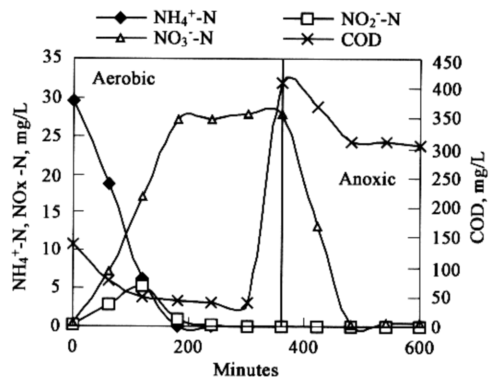

Fig.2 Nitrogen removal in SBR1

2.2 Nitritation by adding NaCl

After steady-state performance was well established, various loadings of NaCl were applied to explore nitrite accumulation. As shown in Fig.3, salt levels applied in influent effect the NO_2^-/NO_x^- ratio and the duration needed to obtain high nitrite build-up. The NO_2^-/NO_x^- ratio increased with salt application time and salt level. Comparison with low addition dose of salt, slug dose of salt avails to obtain high

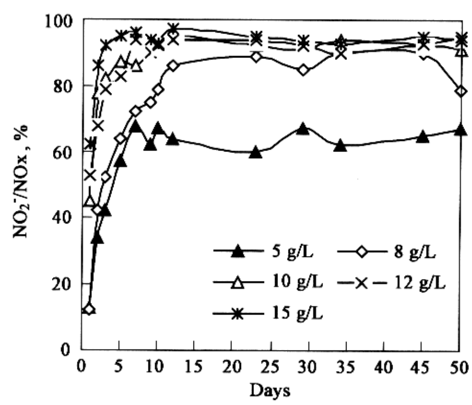

Fig.3 Effect of salt dosage on NO_2^-/NO_x^-

NO_2^-/NO_x^- ratio with reduced inhibition time. Despite of applying as long suppress time as possible, low salt concentration such as 5 g/L could not obtain over 90% nitrite build-up rate. Taking cost and performance into considerations, the optimum salt level applied to achieve nitritation is 10 gNaCl/L, and recommend salt application duration is no less than 20 d.

Fig. 4 and Fig. 5 depicts variations of dynamic of nitrogen at the first and second day after applying 10 g/L salt, respectively. Effective inhibit was achieved immediately as a result of NO_2^-/NO_x^- ratio increasing from 22% at the first day to 88% at the second day. However, enough salt inhibit time had to be applied in order to qualify successful enrichment of ammonium-oxidizers. The effective salt selection time that ensures nitrite-oxidizers to be washed out is over 20 d in this experiment. In order to establish an optimum salt dosage that can selectively inhibit nitrite-oxidizers but do not be severely detrimental to ammonium-oxidizers, nitrification was explored when applying different dosage of salt(Fig.6). Ammonia nitrogen removal efficiency and nitrification rate decreased sharply when applying over 10 g/L salt, which was severely detrimental to the growth of ammonium-oxidizers. Base on cost and effectiveness considerations of little salt effect, the optimum dosage of salt was also established to be 10 g/L.

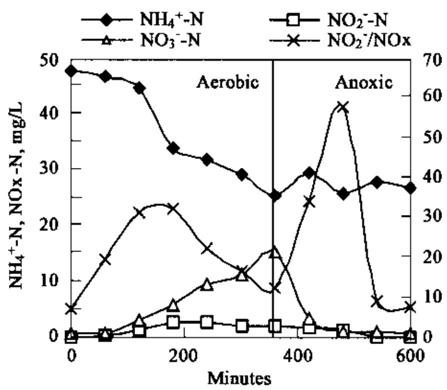

Fig.4 Cycle dynamic at the first day of applying 10 g/L salt

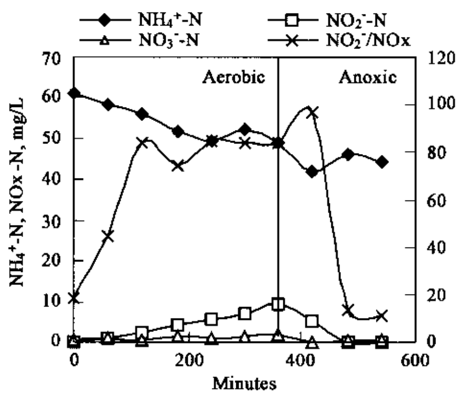

Fig.5 Cycle dynamic at the second day of applying 10 g/L salt

During salt addition, two stages(stage Ⅰ to Ⅱ) could be compartmentalized according to corresponding responses. At stage Ⅰ, which can be named as acclimation period, biomass in SBR treatment receiving saline waster acclimatizes itself to salt. Salt addition lays great shock on systems to

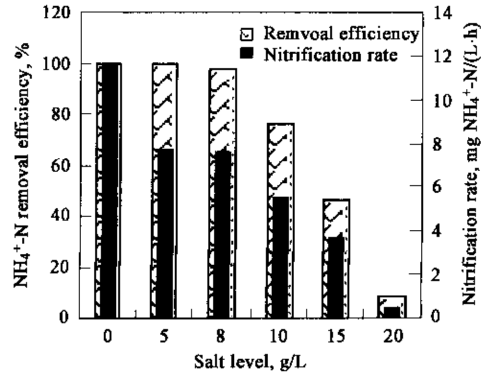

Fig.6 Effect of salt on nitrification

break out the steady state with phenomena such as decreased ammonium removal rate and elevated effluent ammonium concentration. A notable observation is that nitrite accumulation rate increases and ammonium removal efficiency becomes stable as inhibition time increases. At stage Ⅱ, called as stable inhibitory period, with the same influent salt concentration as stage Ⅰ, SBR stayed stable ammonium removal rate and ammonium removal efficiency. This stage is of importance that provides effective salt selection time that ensures nitrite-oxidizers to be washed out since salt puts on a stronger selection stress on nitrite-oxidizers than ammonium-oxidizers. Loss of ability to grow in the presence of salt might be attributed to changes in species predominance.

2.3 Maintain nitritation by controlling aeration duration

Maintaining strategy to deter growth of aerobic nitrite oxidizers has to be applied after the majority of nitrite-oxidizers was washed out of treatment system and after stopping addition of inhibitors. In such system as ammonium-oxidizers predominates, one possible strategy is stopping aeration immediately after ammonia bas been completely oxidized. The reason can be explained by data depicted in Fig.7, which showed the results at the day 18 after achieving nitritation by 30 d addition of 8 g/L salt. Due to successful enrichment of ammonium-oxidizers, the nitrite concentration is at the maximum when the ammonium concentration was completely oxidized. Prolonged aeration, however, contributed to oxidation from nitrite to nitrate. The complete ammonia oxidation corresponded exactly to the valley in the pH versus time graphic, so using pH can offer a possibility of stopping the aeration just after complete removal of ammonia.

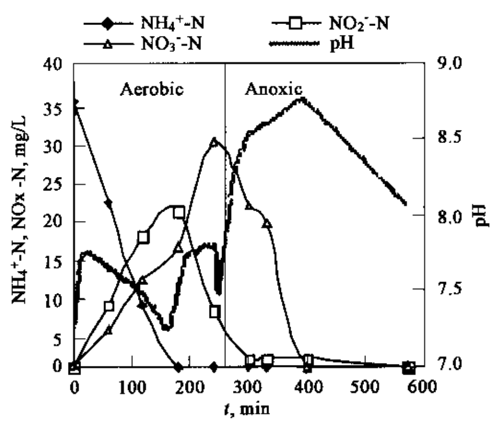

Fig.7 Evolution of pH and nitrogen in a cycle

After 20 d stage Ⅱ (stable inhibitory period), salt addition stopped and fresh domestic wastewater was applied again. The feasibility and validity of maintaining nitritation by controlling aeration duration was established by experiments(Fig.8). Ammonium removal efficiency obtained completely recovery in comparisons with the performance before salt addition. Despite of no salt inhibition, over 90% NO_2^-/NO_x^- ratio can be maintained due to successful washout of nitrite-oxidizers at stage Ⅱ (Fig. 8a and Fig. 8b). However, conversion from shorter nitrification-denitrification to full nitrification-denitrification was observed at the day 45 in SBR operated by fix-time mode(Fig.8a). Comparison with SBR by fix-time mode, over 94% NO_2^-/NO_x^- ratio was maintained during 80 d experiment in SBR applying real-time control of aeration time(Fig.8b). Control of aeration time is significant to hold nitritation after successful washout of nitrite-oxidizers. It is clear through experiments that holding nitritation by control of aeration time can be realized.

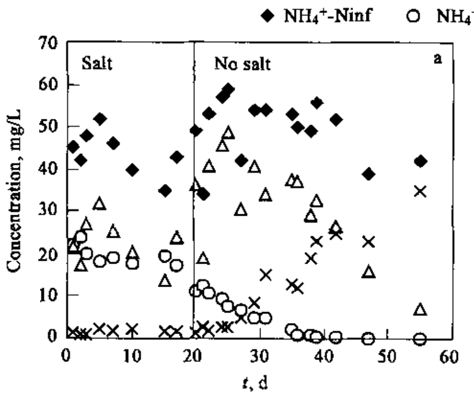

Fig.8 Influent ammonium concentration and ammonium, nitrite and nitrate concentration after nitrification in SBR1(a) and SBR2(b) during research

2.4 Evaluate the methods

It is well established in literature that nitritation could save energy and electron donor, provided nitrification could be stopped at nitrite. Until recently, holding the nitrification at that intermediary level was not successful. How to achieve wash out of nitrite-oxidizers is the key to successfully hold the nitrification ending as nitrite. By implementing salt inhibition, successful enrichment of ammonium-oxidizers was achieved. The principle is based on the diference in tolerance of salinity between ammonium-oxidizers and nitrite-oxidizers. According to the results, ammonium-oxidizers have a better tolerance of salt than nitrite-oxidizers. High salt concentration, where the growths of nitrite-oxidizers are almost suppressed, offers a selective advantage to ammonium-oxidizers. Compared with other methods, one of predominance is to achieve stable nitritation under normal process conditions.

During salt addition, the performance of the three systems got upset with phenomena such as decreased chemical oxygen demand and ammonium removal efficiency, increased effluent suspended solids and much solid washout, etc. However, when systems were allowed to return to the original conditions after salt addition, their performance can recuperate providing some recovery time was applied.

Although the real-time control strategy is validated on SBRs, the addition of sodium chloride to achieve nitrite build-up and the principle of nitrification duration control to prevent the growth of nitrite-oxidizers can also be applied to continuous flow configurations. The optimal SBR phase scheduling on pH measurement allows to further saving cost and energy. It is simple, inexpensive and applicable, especially for coastal city, where seawater can be utilized to achieving nitrite accumulation.

3 Conclusions

The biological nitrification/denitrification via nitrite can be achieved by applying dosage of NaCl. The strategy utilizes salt as selective inhibitor of nitrite-oxidizers to achieve nitrite build-up. In order to wash out nitrite-oxidizers and enrich ammonium-oxidizers, over 20-day salt inhibit need to be applied. The high nitrite accumulation is highly dependent on the salinity in influent and the application duration of salt. The optimum dosage of salt was established to be 10 g/L. Although during salt inhibition treatment performance was upset, performance can be recuperated after salt addition. Maintaining strategy to deter growth of aerobic nitrite oxidizers was developed by controlling aeration duration using pH as control parameters.

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(Received for review December 13, 2004. Accepted March 24, 2005)