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Nitrogen removal in sequencing batch reactor*

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Abstract — This article introduces bio-denitrification rule of several operation in SBR system. The results show that sequencing aeration in SBR meets the needs of oxic and anoxic conditions of bio-denitrification, and it is a promising bio-denitrification technique. It is the first discover that during the treatment of brewery wastewater, when the brewery wastewater is added in the activated sludge, its denitrification rate is faster than methyl alcohol added. This experimental result has great significance. It is suggested that adding original brewery wastewater shall be first considered in bio-denitrification of several kinds of wastewater. Alternative operation of aeration and mixation, namely nitrification and denitrification, has high denitrification efficiency.

Keywords: SBR; aeration; nitrification; denitrification.

1 Introduction

In general, through bio-treatment, urban and industrial wastewater still has a large amount of ammonia-N. Ammonia-N not only does harm to fish and other water resources and further consumes DO but also reacts with chlorine, synthesizes chloramine to decrease disinfection. It has gained more attention that ammonia-N and phosphorus cause eutrophication in lakes, gulfs and reservoirs, produce great dangers to environment. In recent years, further denitrification and phosphorus removal based on the secondary treatment of wastewater is always the focus of research and technology application in the world.

After research and practice for a few years, people gradually recognize that among the ways of denitrification and phosphorus removal, biological treatment is the cheapest and the most promising way. If either nitrogen or phosphorus lacks, eutrophication does not occur. This article only deals with biological denitrification. Now activated sludge treatment is dominant in biological denitrification, such as A/O, A/A/O, AB, SBR. All of these means obey the following essential theory: under oxic

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condition, nitrobacteria and nitrousbacteria and other autotrophs complete the nitrification, then under anoxic condition, denitrification is finished by facultative heterotrophic bacteria. In this bio-chem process, the forms of nitrogen are showed in Fig.1 (Alleman, 1980). It could be seen that the shift of oxic and anoxic condition is the necessary environmental condition for denitrification. Sequencing batch reactor activated sludge process (abbreviated as SBR), not only has advantage such as secondary sedimentation and sludge return are not needed, bio-driving force is large and sludge bulking does not occur, and is famous for simple, lowcost (Melcer, 1987; Palis, 1985), but also is an alternative process of oxic and anoxic and can easily meet the bio-denitrification environmental condition. So, after 1985, research on SBR denitrification is a new focus in bio-denitrification technology development (Allemen, 1980; Palis, 1985).

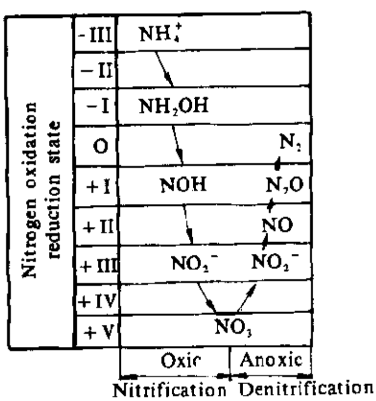

Fig.1 The bio-chem change of nitrogen state in nitrification and denitrification processes

2 Nitrification of limited aeration and denitrification of adding original carbon source

SBR is a cyclical wastewater treatment process which includes fill, react, sedimentation, decant and idle. The main equipment has two functions: aeration and secondary sedimentation. Sludge return is not necessary. Process is very simple. Limited aeration operation is that when wastewater passes primary sedimentation tank into reactor, aeration does not occur (limited aeration); when wastewater reaches the effective volume of reactor, aeration begins (react), organic utilization and nitrification occur in this phase; when it reaches the predictive water quality, aeration stops, water sludge separation and sludge concentration occur in the reactor, at this time, reactor is used as secondary sedimentation tank; then, clear supernatant is drained; finally, waste sludge is discharged, too. One cycle finished. The only difference between the limited and unlimited operation is that in the latter operation, aeration begins when wastewater enters the reactor. The reactor in this experiment is cylindrical equipment made from organic glass. Effective capacity is 14.3 litres, a circular diffuse airplate is installed at the bottom, ten sample cocks are equipped on one facet of the reactor, which served as sample analysis, decant and sludge discharge. Many environmental factors have great influence on nitrification and denitrification, such as temperature, pH, alkalinity, DO etc. In order to research denitrification rule under the same condition, temperature controller is used to keep the reactor temperature at 20±0.5°C. When aeration operated, the dissolved oxygen in the reactor remains 2 mg/L. When denitrification begins and aeration stops, full stir will be needed. The matters to regulate pH and alkalinity are not added. The above way can make every kind of denitrification experiment operate under the same condition and the same starting-point, thus benefits plan comparison and research.

2.1 Nitrification of excessive TKN in wastewater

Sludge age of SBR system aiming at organic removal is very short, and nitrification does not occur. Basing on the activated sludge which grows on brewery wastewater, the sludge age and nitrogen concentration in wastewater is increased. After organic nitrogen turns to ammonia-nitrate (shows as NH_4^+ , NO_3^-), aeration continues. Through ten cyclical operations, a large amount of nitrifying bacteria grows, NH_4^+, is oxidized to NO_3^-, then nitrification experiment is carried on. Brewery wastewater is still used as substrate. Excessive nitrogen and phosphorus are added. At the end of filling in limited aeration, namely the beginning of aeration, COD (COD_{cr}) and total phosphorus (*Pt*) concentration are 349 and 8.18 mg/L respectively, pH is 6.94. Fig. 2 shows the original concentrations of NH_4^+-N; organic-N and NO_x^--N, and their variation with respect to the aeration time. At the beginning of aeration, COD and TKN concentration are 349 and 85 mg/L respectively, nitrogen is excessive. In spite of these conditions, the utilization percentage of TKN is 89%, when aeration time is 12 h, the nitrification rate of SBR is fast. At the previous three hours of reaction, NH_4^+-N concentration increases. The reason for this is that the ammonification rate of organic-N is faster than the nitrification rate of NH_4^+-N, which makes NH_4^+-N accumulate; from then on, org-N and NH_4^+-N concentration greatly decreases with reaction time, but NO_x^--N increase, their variation rate changes smaller and smaller.

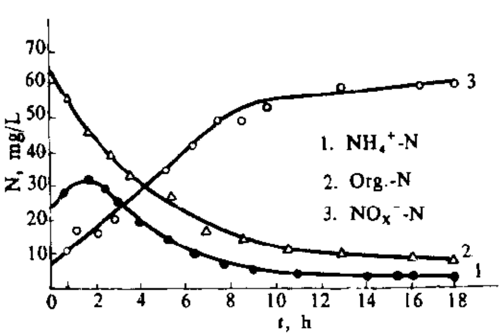

Fig.2 The change state of nitrogen in nitrification phase

2.2 Denitrification of brewery wastewater and methyl alcohol used as org-C source

The composing rate of bacteria is very slow under anoxic condition. So the nitrogen removed by denitrification through assimilation is very small. Most of nitrogen is removed as N_2 through disassimilation. In denitrification phase, either added org-C or dissolved through microorganic internal inspiration can be utilized. It is considered that the latter denitrification rate is smaller. However methyl alcohol is easier to utilize and its price is cheaper, it can usually be used as organic carbon source and electron donor. The equation is:

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O - 6OH^-.$$

It can also be showed through experiments that the denitrification rate is faster when methyl alcohol is served as org-C source.

Denitrification experiments of adding org-C have been done. Although methyl alochol has above advantages, this method belongs to adding dose after all and its long-term operation is very expensive. So with methyl alcohol and brewery wastewater served as organic carbon respectively, denitrification efficiency of two different carbon sources and different organic concentration has been researched. Under the other same experimental condition, the same four reactors have the same mixture liquor that has completed nitrification, different quantity of methyl alcohol and brewery wastewater are added in the same time, then magnetic stirrer is used to control anoxic condition and parallel experiment is done (Fig.3).

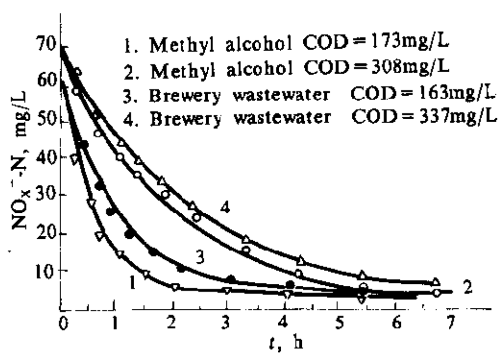

Fig.3 Denitrification of different concentration methyl alcohol and brewery wastewater served as org-C source

After four parallel experiments reaction for six hours, it could be seen that original NO_x^--N concentration decreases from 69 mg/L to 4 mg/L. Denitrification efficiency is 94% – 98%. The above data illustrates that denitrification rate and efficiency are higher than that of nitrification, denitrification reaction is easier to operate than nitrification for the same organic matter, though denitrification rate is higher with respect to the high original organic concentration, this effluence is not great when COD is no less than 160 – 170 mg/L. But it should be mentioned that the most important discovery in this research is that under the experimental conditions, denitrification rate of brewery wastewater served as org-C source is much higher than that of methyl alcohol (Fig. 3). After four-hour-reaction, the former denitrification efficiency is 85% – 95%, the latter (adding methyl alcohol) is about 82%. In the first two hours, the difference is very large.

This discovery has much practical significance to the bio-denitrification of certain wastewater. The reason for this is that adding original wastewater as org-C in denitrification not only can avoid adding methyl alcohol and spare operate cost but also can make treatment system utilizing organic compound in denitrification phase, which can increase treatment capability. But further research shall be made on what kind of wastewater having these characteristics.

The experiment results that the denitrification rate of adding brewery wastewater is faster than that of methyl alcohol can be explained. A lot of facultative bacteria exist in ordinary activated sludge. In limited aeration SBR system, the proportion of facultative bacteria is much large. Because under oxic condition these facultative bacteria have adapted to the organic compound of brewery wastewater and these organic compounds are easy to utilize. So under anoxic condition, these facultative bacteria are easy to receive organic compounds of brewery wastewater as carbon source of denitrification. Meanwhile using NO_3^- as electron accepter can accelerate denitrification rate. Although methyl alcohol is early to utilize, as far as these facultative bacteria that use brewery wastewater as substrate under oxic condition, methyl alcohol may be strange to them. This phenomenon gives us an important revelation: For biodenitrification of easily utilized wastewater, using original wastewater as organic carbon source in denitrification shall be first considered. Even if sometimes its denitrification rate and effieicncy are slower than that of adding methyl alcohol, the full economic technology analysis shall be made. That is to say using waste to manage waste. Certainly, for bio-denitrification of difficult-utilized wastewater, optimal plan and coefficients should be determined through experimental tests.

In denitrification phase, the bio-denitrification technology of continuous fill, such as A/O, only the internal cycle ratio of nitrification liquor is at least as five times as that of fill can make denitrification efficiency higher than 80%. Much higher cycle ratio can prevent anoxic tank from keeping anoxic condition. But in SBR system, the operations of nitrification and denitrification are just in the order of sequencing and stopping aeration. Internal cycle is not needed. Such denitrification can not only keep the excellent anoxic condition but also make denitrification operation thoroughly. After denitrification, short time aeration may be beneficial to utilizing the rest organic matter and blowing the gas produced in denitrification (then goes to sedimentation phase and drain treated waste), which is another advantage of SBR denitrification.

3 Bio-denitrification of three different operation modes while organic carbon source is not added

dissolved

in internal respiration phase as carbon source of denitrification, can spare dose cost and decrease waste sludge through internal respiration. SBR unlimited aeration can remove organic matter by aeration in fill phase. It can also raise treatment capability and shorten the cycle time. In addition, because filling of SBR is sequencing, secondary sedimentation tank and sludge return are not necessary, only one reactor is needed, SBR operation is very flexible. Aeration or not, stir and operation time may be controlled arbitrarily. Basing on this idea, nitrification and denitrification research on three different operation modes and the controlling means of three same sequencing reactors have been made, as shown in Table 1. In three different operation reactors, temperature, DO, pH, mixture concentration and other environmental factors are the same. COD and NH_4^+-N of fill is lower than previous experiments. They are 244 and 24 mg/L respectively.

When wastewater reaches the effective depth of water, activated sludge concentration is 3500 mg/L. Higher sludge concentration helps internal respiration and dissolving enough organic to serve as carbon and power sources in denitrification phase. In former phase of the experiments, the effluent of every other half an hour are sampled. In latter phase, the effluent of every other an hour are sampled.

Table 1 Three operation modes of no adding org-C

Operation mode	Filling mode and lasting time	Operation controll of filling phase	Operation control of react phase
I	Continous and uniform; fill for three hours	Alternate operation of aeration and stir for 30 minute	Alternate operation of aeration and stir for 30 minute
II	Continous and uniform; fill for three hours	Aeration	Nitrification: aeration denitrification: stir
III	Fill instantly		Nitrification: aeration denitrification: stir

The experimental results of three different operating modes are shown in Fig.4. In general, these three different operating modes of no adding org-C, all of them can make NH_4^+-N and NO_x^--N concentration less than 2.0 and 1.0 mg/L respectively. The denitrification percentage of I, II, III operation mode reaches more than 92% after reaction for 7, 15, 9 h respectively. It can be seen, though these three modes got all satisfactory denitrification rate, efficiency is different by far.

The II, III modes spend 7 and 3.5 h respectively to decrease NH_4^+-N

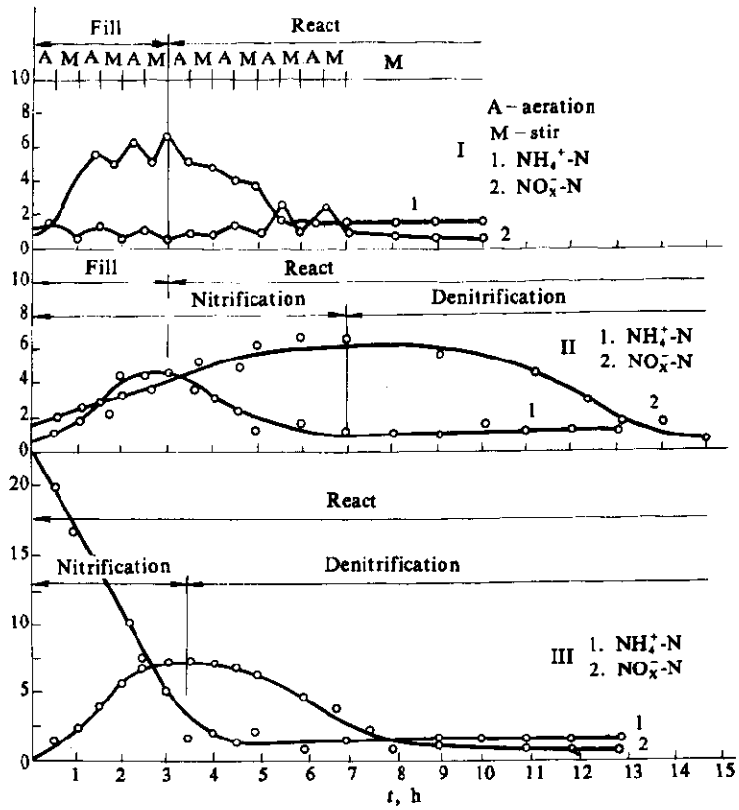

Fig.4 Bio-denitrification experimental results of three different operation modes

concentration from 24 mg/L to 1 mg/L, NO_x^--N increase from 1 mg/L to 7.5 mg/L. The nitrification has been finished satisfactorily. It is seen that most of NH_4^+-N is used to make metabolism. These two modes spend 8 and 5.5 h respectively. The NO_x^--N concentration decreases from 7.5 mg/L to below 1 mg/L. Though the denitrification is completed thoroughly, they are much lower than the previous experimental results. Those results are carried out under the following condition: original NO_x^--N concentration is 69 mg/L when brewery wastewater and methyl alcohol are added in the experiment. The experiments take 4 and 6 h to reach the denitrification efficiency, which is more than 90%. That is to say, in the practical operation of bio-denitrification, adding original wastewater shall be first considered. In unfortunate condition, adding methyl alcohol is mecessary, because such way can greatly accelerate denitrification rate, shorten reaction time and decrease the reactor volume.

In II operate mode, because of continuous fill for three hours and aeration at the meantime, in the first two hours, the utilizing NH_4^+-N rate of nitrification and metabolism is lower than the filling NH_4^+-N rate, so NH_4^+-N concentration increases constantly. But in the third hour, the two factors reach the balance, the NH_4^+-N concentration changes little. At the end of fill, NH_4^+-N decreases constantly. But NO_x^--N concentration increases in fill and nitrification phase, decreases in denitrification phase. III Mode completes fill phase instantly, the change of NH_4^+-N and NO_x^--N concentrations obeys the ordinary rule.

Compared with two modes, the denitrification efficiency of I mode is the highest. It only takes seven hours to complete nitrification and denitrification processes. In the first hour of the three continuous filling, NH_4-N concentration increases constantly. In the later two hours, it decreases with respect to aeration (nitrification), but increases with stir (denitrification). At the end of fill, it decreases constantly. But in mixture phase, its decreasing extent is very small. NO_x-N concentration increases with aeration and decreases with stir during the alternation of aeration and stir, which appears regular change. That nitrification and denitrification alternates with aeration and stir can be seen from the theory and experimental result of this operate mode. Although organic carbon is not added, brewery wastewater exists constantly. In fact, this phenomenon also proves the advantage that brewery wastwater can be used as the organic carbon of denitrification. These are three reasons for the high denitrification efficiency of mode I. First, in denitrification phase, there is enough brewery wastewater used as carbon and power sources. This means organic matter is added in ordinary bio-denitrification. Second, because aeration and stir alternately operate after filling, organic concentration in the reactor is high in most denitrification phase. This undoubtly accelerate denitrification rate. Third, alternate aeration not only provides NO_3^- for denitrification, but also promptly blows the gas from the reactor produced in the previous denitrification such as N_2, CO_2, NO_2. This means that the producer concentration of denitrification is removed steadily, which helps accelerate the later denitrification rate. This operating mode shall be further researched and developed in order to be applied in the practical bio-denitrification engineering.

4 Conclusion

SBR sequencing aeration just meets the demand of oxic and anoxic condition in bio-denitrification phase and internal recycle used in continuous bio-denitrification phase and internal recycle used in continuous bio-denitrification is not needed. This makes nitrification and denitrification have high driving force and reaction rate and makes denitrification operate thoroughly. It is a promising bio-denitrification technology.

Among these different operation modes, denitrification operates more thoroughly than nitrification. Denitrification rate of adding organic carbon is faster than that of no adding organic-C.

Conventional viewpoint is that when methyl alcohol is used as organic carbon, the denitrification rate is the highest. As far as the active sludge bred under our experimental condition, the denitrification rate of adding brewery wastewater is faster than that of adding methyl alcohol. This discovery is very significant to bio-dentrification process. Original wastewater used as organic-carbon source can not only spare the cost of adding methyl alcohol, but also make treatment system to utilize most organic matter in denitrification phase, thus, the author suggest that in the design and operation of bio-denitrification process, adding original wastewater as organic carbon of denitrification shall be first considered through experiments.

In the denitrification experiments of no adding organic carbon, the alternative operation mode of aeration and mixation has high denitrification efficiency. The essence of this mode is that the alternation of nitrification and denitrification makes the reactor have enough brewery wastewater used as org-C source in denitrification phase. Alternative aeration not only provides NO_3^- for denitrification, but also blows kinds of gas produced in denitrification, thus accelerates the reaction rate. The operation rate should be researched further.

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