Study of the Effect of Various Factors on the Nitrosification to Tannery Wastewater

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Abstract: Tannery wastewater has a high level of contamination of ammonia nitrogen. The conventional method to remove ammonia nitrogen is the entire nitrification. While this experiment used the nitrosification, which had some merits, such as reducing the amount of alkali, decreasing the supply of oxygen and saving carbons. In this paper, removal of the ammonia nitrogen in tannery wastewater by the method of nitrosification was investigated. Some influence factors such as temperature, pH, dissolved oxygen (DO), aeration way and C/N on the nitrosification to the tannery wastewater were studied in a sequencing batch reactor (SBR). The processes showed that the nitrosification to the tannery wastewater could be achieved by intermittent aeration. The results indicated that the nitrosification had better effects comparatively when the temperature was 31±1℃ and the pH was 7.8-8.2. In addition, it was needed to choose a proper C/N and put the NaOH-$NaHCO_3$ buffer solution into the system to keep the pH in the cycle relatively stable. The results also demonstrated that the concentration of ammonia nitrogen in the effluents was about 20mg/L after the nitrosification process, reaching the national emission standards for secondary effluent and the removal rate of ammonia nitrogen was about 89%, which showed that the nitrosification process was effective for tannery wastewater to remove ammonia nitrogen.

Key Words: tannery wastewater; the nitrosification; ammonia nitrogen

1 Introduction

The pollution of tannery industry is the third largest in the light industry after the food and paper-making. Tannery wastewater has heavy smell, high alkalinity, high chrome and a high level of suspended solid. And the concentrations of COD, BOD, Cl^-, NH_4^+-N and Cr^{3+} are at a high level [1]. The treatment of tannery wastewater is a big problem need to be resolved urgently. In the tannery wastewater, the ammonia nitrogen has a great harm to water. When the wastewater with ammonia nitrogen is discharged into the water, the ammonia nitrogen will bring a large increase of algae and other microorganisms, and induce the eutrophication pollution. It will make a decline in dissolved oxygen in the water, a large number of dead fish and even lead to the demise of the lake when it gets worse. The ammonia nitrogen will also increase the amount of chlorine in water disinfection and industrial water cycle sterilization, which will make difficulties to the water treatment factory and cause the smell of drinking water. This study focused on the removal of ammonia nitrogen in tannery wastewater.

The conventional method to remove ammonia nitrogen is the entire nitrification, the typical process of ammonia by nitrification and denitrification is, $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow NO_2^- \rightarrow N_2$. In fact, we can see by the principle of denitrogenation that the oxidation of

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ammonia nitrogen is made up of two independent types of bacteria, in which the process of ammonia converting into nitrite is the key step. But for the denitrifying bacteria, both NO_3^- and NO_2^- may be the ultimate. If ammonia just turns into nitrite but not further into nitrate and then directly denitrifies, it will not only simplify the process but also reduce the amount of alkali, decrease the supply of oxygen and save carbons.

The factors which influence the accumulation of NO_2^- are temperature, the concentration of dissolved oxygen (DO), pH, free ammonia (FA), the concentration of organic compound, etc [2]. In this paper, we discussed the optimum conditions of the nitrosification to tannery wastewater from temperature, pH and C/N.

2 Experimental

2.1 Materials

The wastewater was obtained from the pretreated integrated effluent of a tannery in Shandong province. The concentrations of COD and NH_4^+-N were about 460 mg/L and 200 mg/L respectively, and the pH was 7.5. The concentration of COD need in the nitrosification was small, so the wastewater demanded an anaerobic treatment before entering into the SBR reactor to reduce the concentration of COD. The concentration of COD after the treatment was about 120 mg/L. Because of the anaerobic treatment, some organic nitrogen was turned into ammonia nitrogen, so the NH_4^+-N concentration was increased to 220mg/L.

2.2 Experiment equipments

The SBR reactor was made of plexiglass. The diameter and height were 10cm and 1.2m respectively, and the effective volume was 750mL. The reactor was fixed on the bracket. There were some equal spacing sampling pots set in the vertical direction of the reactor for the sampling and drainage. The sticky sand was used as the micro pore aerator to run blast aeration, the rotameter was used to adjust aeration volume, and the thermometer was used to detect the temperature. The equipment was showed in Fig. 1.

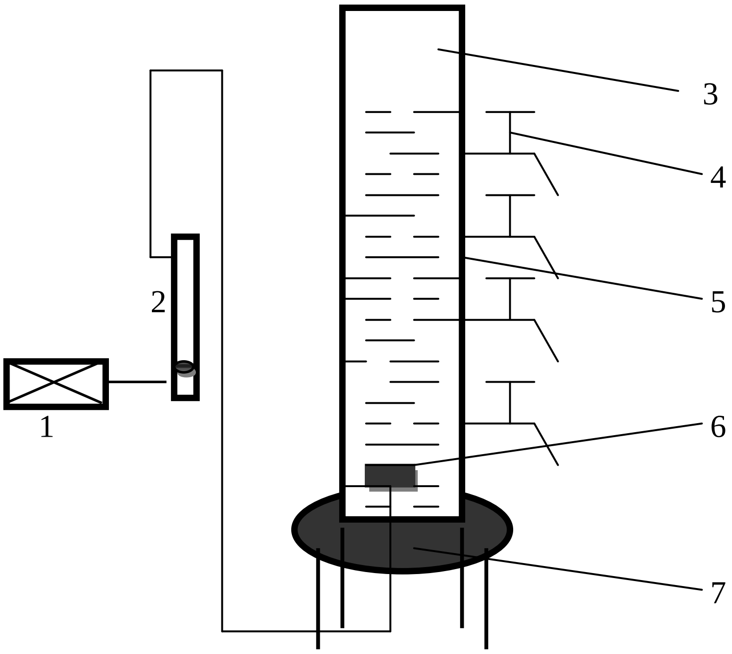

Fig. 1 Experimental equipment

1 aeration pump	2 rotameter
3 thermometer	4 drainage
5 reactor	6 micro pore aerator
7 bracket	

2.3 The main analysis contents and methods

The concentration of NH_4^+-N, nitrite, and nitrate were determined by the Nessler's reagent spectrophotometry, the N-(1-naphthyl)-ethylenediamine spectrophotometric and the phenol disulfonic acid spectrophotometry respectively. The concentration of COD was determined by the dichromate method. The pH and DO were measured by the acidity and dissolved oxygen instruments.

3 Experiment process and discussion of the results

3.1 The initial realization of nitrosification

The operation cycle of the SBR reactor was approximately 6h, 2 cycles a day, with short-time water and intermittent aeration. At the start of the cycle, about 600mL tannery wastewater was put into the reactor. And about 450mL supernatant was discharged after 30min precipitation in the end. The wastewater and the sludge were taken from the same plant, so it took less time relatively to domesticate. The nitrosification was basically achieved after 10 days with the temperature of 31±1℃, the aeration capacity of 0.4L/min and pH of 7.8-8.2. Then the nitrosification rate reached to 60%, as shown in fig. 2.

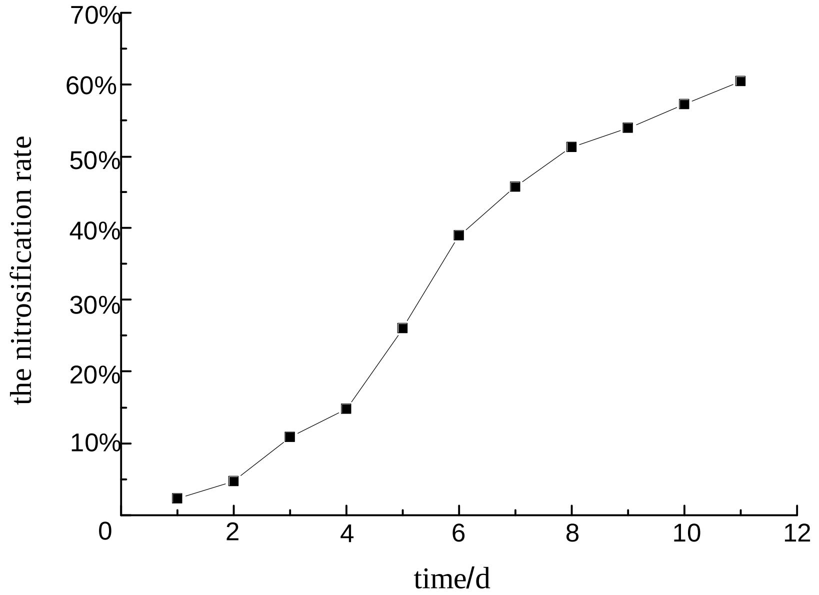

Fig. 2 The change of nitrosification rate in the domestication

The bio-nitrification reaction can be carried out in 4℃-45℃. The nitrobacteria in the activated sludge get more serious inhibition under 12℃-14℃, so it will result in the nitrite accumulation. When it is 15℃-30℃, the nitrite will be completely oxidized into nitrate. And there will be the nitrite accumulation again when it is above 30℃ [3]. In addition, the optimum pH for the nitrite bacteria is 7-8.5, and the nitrobacteria 6-7.5. So we control the temperature, pH and the concentration of dissolved oxygen in the system to provide the more favorable conditions to the nitrite bacteria and to inhibit the growth of the nitrobacteria, then to achieve the nitrosification.

3.2 The influence of aeration on the nitrosification

The way of aeration mainly affects the concentration of dissolved oxygen. Because our instrument is not perfect, without on-line measurement devices, so we can only rely on the rotameter to regulate the amount of aeration, using the dissolved oxygen testing instrument manually.

We studied two different ways of aeration. One was continuous aeration, which was not stop in the entire cycle. The other was intermittent aeration, which was 1 hour aeration and then 30 minutes cessation.

We made the system run for 10 days in the two different ways of aeration, with the temperature of 31± 1℃ and pH of 7.8-8.2. It was found that the concentration of dissolved oxygen in the system was relatively high by continuous aeration even if a small amount of aeration. It could be solved by intermittent aeration. The nitrosification rates by different aerations were given in fig. 3.

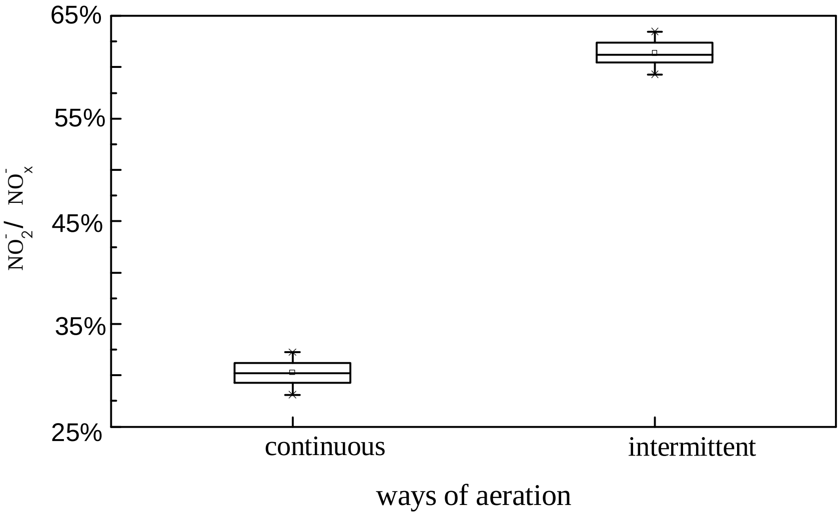

Fig. 3 The nitrosification rates by different aerations

In fig. 3, it was found that the nitrosification degree varied greatly by different aerations. Strictly speaking, the nitrosification didn't come true by continuous aeration for only about 30% nitrite in the effluent. That was because that continuous aeration made the system a higher concentration of dissolved oxygen, generally between 3mg/L-5mg/L. In that condition, the majority of ammonia was completely converted into nitrate and only a small amount of nitrite accumulated. However, intermittent aeration could control the concentration of dissolved oxygen between 0.5mg/L and 2mg/L. In the condition the concentration of dissolved oxygen was lower, the growth of nitrite and nitrate bacteria all decreased, but the decline trend of the nitrate bacteria was faster than that of the nitrite bacteria. That was to say, the nitrite oxidation rate decreased faster than that of the ammonia oxidation rate, which helped to promote the accumulation of nitrite bacteria, limit the growth of nitrate bacteria. It was found that the nitrosification rate was more than 60% by intermittent aeration.

3.3 The influence of temperature on the nitrosification

When the nitrosification of system basically was achieved, the influence of temperature on the nitrification in tannery wastewater was studied. The system ran 10 days separately at the temperature of 25±℃, 31±1℃ and 36±1℃, with the pH of 7.8-8.2 and aeration volume of 0.4L/min. Then the concentrations of nitrite and nitrate in the effluent were determined. The optimum temperature for nitrification to tannery wastewater could be observed by comparing the nitrosification rates under different conditions. The operating results under different temperatures were given in fig. 4.

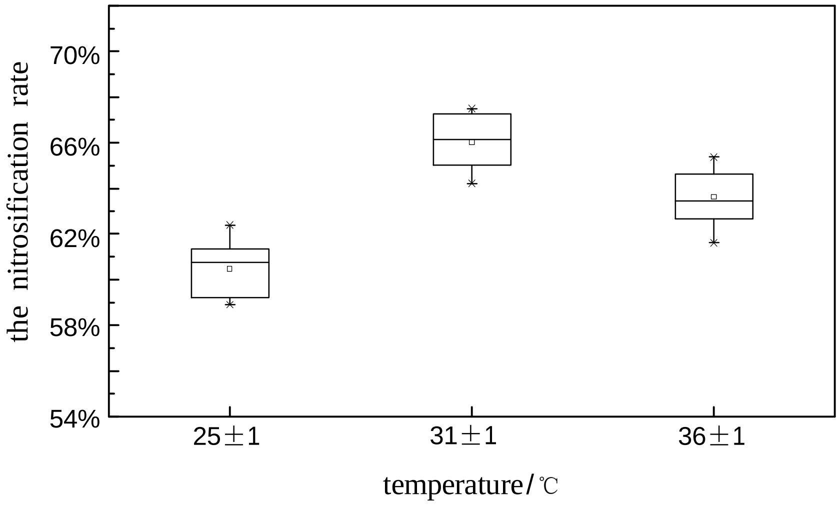

Fig. 4 The nitrosification rates under different temperatures

As shown in fig. 4, the nitrosification rate had a relatively better result under 31± 1℃. That is because that the sensitivity of nitrite and nitrate bacteria to temperature is different. There is an optimum growth temperature for all micro-organisms. At room temperature, the growth rate of nitrite bacteria is less than that of nitrate bacteria, and the nitrite produced from the former can be easily oxidized into nitrate. So at that temperature, only the nitrification can be carried out. When the temperature exceeds 30℃, the growth rate of nitrite bacteria will be faster than that of nitrate bacteria and be in a dominant position in the system. Raising the temperature and utilizing the different temperature effects of the two kinds of bacteria can induce the accumulation of nitrite bacteria and then achieve the nitrosification. However, the higher temperature is not the better, because rising temperature will lead to the denaturation of protein and then result in the decrease of reaction rate. Also heating the wastewater needs energy, the higher the temperature, the greater the energy consumption.

3.4 The influence of pH on the nitrosification

After the optimum temperature was found, the influence of pH on the nitrosification to the tannery wastewater was studied. The system ran 10 days separately at the pH of 7.3-7.7, 7.8-8.2 and 8.3-8.7, with the temperature of 31±1℃ and aeration volume of 0.4L/min. The optimum pH for nitrosification was investigated by comparing the nitrosification rate under different conditions. But at the beginning, we focused only on the original pH without thinking of the change of it in the system, though the system basically achieved nitrosification, the nitrosification rate was lower. The operating results under different pH were given in fig. 5.

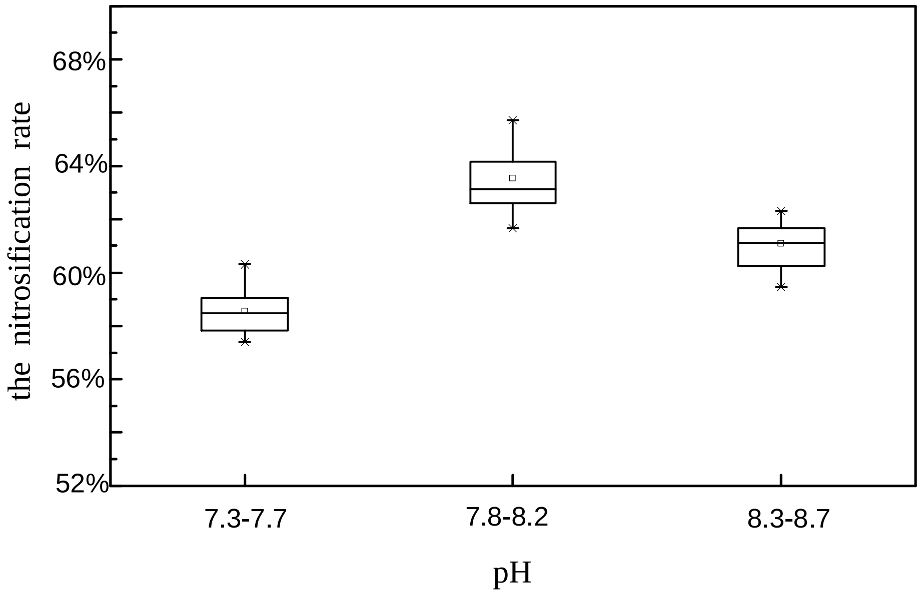

Fig. 5 The nitrosification rate under different pH

It could be found in fig. 5 that when the pH was 7.8-8.2, we could get a relatively better result of the nitrosification rate. That is because different bacteria have different optimum pH. By controlling the pH in the appropriate range, we can inhibit the activity of nitrate bacteria and get a large number of accumulations of nitrite. The pH suitable for most bacteria is 6-8, for nitrite bacteria is 7.0 -8.5 and for nitrate bacteria is 6.0-7.5 [4]. Someone also said that the best pH for nitrosification was 7.8, 7.9 [5]. The optimum pH of the nitrosification investigated in our experiment was 7.8-8.2. However, it could be observed that the nitrosification rate was only about 66% even in the best condition. The reason was that we only noticed the pH at the beginning but ignored that along with processing, and the acid produced in the system consumed the alkalinity. When the pH in the system was lower than 7, the nitrosification would be inhibited.

As the nitrosification rate in the system had not improved, we tested the pH of the effluent and found that the pH in the system at the end of the cycle reduced to 5.5-6.0, which was far from the optimal pH for nitrite bacteria. Therefore we improved the scheme to focus on the change of pH in the cycle. The NaOH-$NaHCO_3$ buffer solution was added into the system to keep the pH in the cycle almost unchanged. The pH was tested irregularly to ensure it in our expectations. The operation results after adjusting were shown in fig. 6.

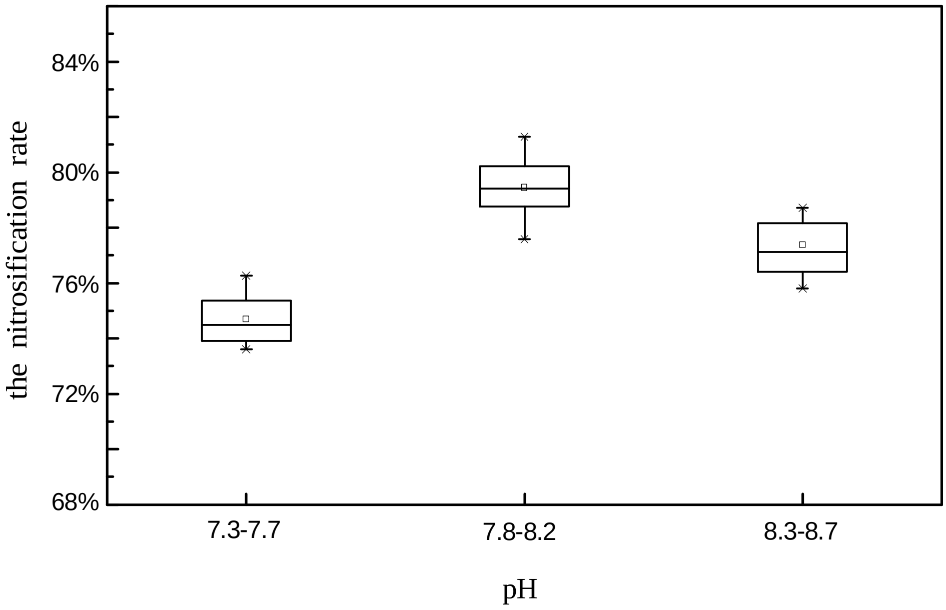

Fig. 6 The nitrosification rate under different pH after adding the buffer solution

It was found in the fig. 6 that all nitrosification rates increased to more than 73% after adding the buffer solution. It was more than 80% when the pH was 7.8-8.2. That was resulted from that the relatively stable pH provided the nitrite bacteria a stable living environment. It could be seen that it was important to keep the pH unchanged to ensure the accumulation of nitrite in the system.

3.5 The influence of C/N on the nitrosification

It was found from the above discussion that the nitrosification rate reached only 80% even in the best condition. It also referred that the anaerobic treatment was run at first because the C/N was low in the references. However, the nitrosification rate was not very good, so we tried removing the anaerobic treatment to improve the C/N. The operation result was shown in fig. 7.

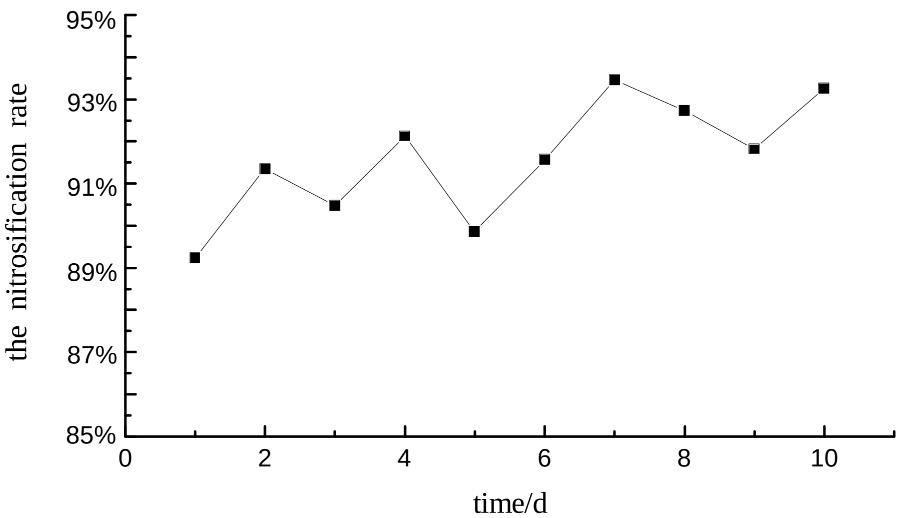

Fig. 7 The nitrosification rate after improving C/N

It could be found in fig.7 that the nitrosification rate could reach 90% after increasing the C/N. The reason was that the lower original COD concentration in the system couldn't provide adequate nutrition so that the bacteria relied only on endogenous respiration to maintain normal metabolism. Improving the C/N could increase the reaction rate, shorten the reaction time and improve the nitrogen removal. However, the COD concentration could not be too high. If it was too high, the growth rate of aerobic heterotrophic microorganisms was far greater than that of autotrophic nitrifying micro-organisms, so that heterotrophic bacteria was stronger in the competition for dissolved oxygen than nitrobacteria. Therefore the effluent would fall flat when the nitrobacteria were inhibited because of the insufficient dissolved oxygen concentration [6].

3.6 The results of removal rate of ammonia nitrogen under the optimum conditions

The optimum conditions were found through above discussion for nitrosification to the tannery wastewater, which were intermittent aeration, suitable C/N, temperature 31± 1℃ and pH 8.2-8.7. The system ran more than 20 days under those conditions and the removal rate of ammonia nitrogen was investigated. The removal rates of ammonia nitrogen in the system were shown in fig. 8.

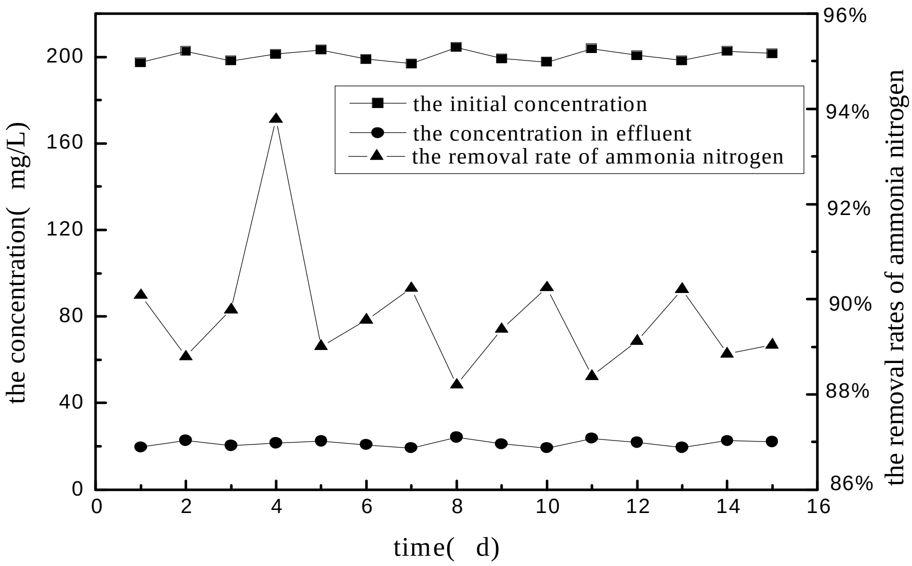

Fig. 8 The removal rates of ammonia nitrogen under the optimum conditions

It could be seen in fig. 8 that the concentrations of ammonia nitrogen in the effluents were about 20mg/L and the removal rates of ammonia nitrogen were about 89%.

4 Conclusions

The nitrosification to the tannery wastewater could be achieved by intermittent aeration. And the optimum temperature and pH were 31±1℃ and 7.8-8.2 separately. At the same time, it was important to keep the pH relatively stable in the system. In addition, it was necessary to adjust the C/N according to the fact. The results demonstrated that the concentrations of ammonia nitrogen in the effluents were about 20mg/L after the nitrosification process, reaching the national emission standards for secondary effluent and the removal rates of ammonia nitrogen were about 89%, which showed that the nitrosification process was effective for tannery wastewater to remove ammonia nitrogen.

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