Study on Treatment of Low Nitrogen Concentration Water by Immobilized Microbial Technology

Ming Sui, Yonglin Guan, Chongjun Zhang, Keyong Zhu and Wenxi Yue
Sichuan Technology and Business College, Sichuan, Dujiangyan, 611800, China

Abstract. In this paper, the high-density denitrifying bacteria on the immobilized carrier after acclimation were used to carry out batch experiments under different carbon source types, carbon-nitrogen ratios, temperature and pH conditions, and the process was investigated for low-concentration micro-polluted water sources. The treatment effect, as well as the kinetic characteristics of nitrogen removal and the nitrogen conversion pathway.

1. Introduction
With the strictening of major sewage discharge indicators and the increasingly serious problem of water eutrophication, it is urgent to further denitify the secondary effluent from deep purification of urban sewage plants. [1-4] some scholars have carried out deep denitrification through denitrification biofilter. The study yielded a nitrate removal rate of 80% to 88%. In this experiment, combined with immobilized microbial technology, the carrier of domestication of denitrifying bacteria under anaerobic conditions was used to investigate the removal characteristics of nitrate in the water by functionalized macroporous FPU carrier immobilized microorganisms at low nitrogen concentration. [5-9] In the experiment, the conventional organic matter was used as the carbon source to study the treatment effect of the process on the low-carbon nitrogen concentration micro-polluted water, and the effects of carbon source, carbon-nitrogen ratio, nitrate nitrogen concentration, HRT, temperature and pH on the denitrification effect were investigated. Influence, through the batch experiment to obtain the ideal carbon source and carbon-nitrogen ratio and optimal regulation of operating parameters, to explore the denitrification kinetics and nitrogen conversion pathway of low-nitrogen micro-polluted water in this process. [10] Finally, the process engineering is enlarged to carry out the test operation of the device, which provides the theoretical basis and design basis for the removal of nitrate and nitrogen in urban micro-polluted water.

2. Experimental principle
The experimental method uses the FPUFS macroporous functional carrier to acclimate and fix the denitrifying bacteria by artificially simulating a low concentration micro-polluted water source, and the domesticated immobilized microbial carrier is added to the reaction system to study the carbon-nitrogen ratio and temperature. The influence of process parameters such as pH and denitrification process on denitrification kinetics. In the absence of oxygen, denitrifying bacteria use the carbon source in the system to make NO$_3^-$ and NO$_2^-$ the final electron acceptor for respiration, and reduce nitric acid to nitrogen (N$_2$), which is called denitrification or denitrification.

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2
\]

\[
\text{C}_6\text{H}_12\text{O}_6 + 12\text{NO}_3^- \rightarrow 6\text{H}_2\text{O} + 6\text{CO}_2 + 12\text{NO}_2^- + \text{energy}
\]

\[
5\text{CH}_3\text{COOH} + 8\text{NO}_3^- \rightarrow 6\text{H}_2\text{O} + 10\text{CO}_2 + 4\text{N}_2 + 8\text{OH}^- + \text{energy}
\]
This reduces nitrogen, nitrous oxide and total nitrogen in the system.

3. Carrier material
The patent carrier FPUFS was added to each reactor in the bioreactor system, and the internal cavity of the carrier is shown in Fig. 1.

![Carrier hole × 500 times](image)

The functionalized carrier is a chitosan and a powdered activated carbon which are added during the synthesis of the polyurethane flexible foam, and are foamed, granulated, opened, and crosslinked to form a polyurethane macroporous network and a chitosan and a glutamic acid coated with activated carbon. A polymer interwoven with an aldehyde or epichlorohydrin or chloroacetic acid crosslinked microporous network. The specific parameters of the carrier are shown in Table 1.

FPUFS contains reactive groups such as hydroxyl, epoxy and amide groups. It has a well-developed microporous structure and good anti-aging properties, abrasion resistance, biocompatibility and deformation. In the experimental study, the individual carrier size was about 20 mm x 20 mm x 20 mm, and the dosage was about 70% of the reactor volume.

| parameter | Specific surface area /m²·g⁻¹ | Water holding capacity /% | Wet density /g·cm⁻³ |
|-----------|-------------------------------|---------------------------|---------------------|
| value     | 80~120                        | 2300~2600                 | 1.0                 |

4. Determination of total nitrogen and water quality ammonia nitrogen
Reagents: (a). Alkaline potassium persulfate solution: 4.0gK₂S₂O₈ is dissolved in water; 1.5gNaOH is dissolved in water, and after cooling to room temperature, the two solutions are mixed and made up to 100 ml, and placed in a polyethylene bottle for one week. (b). Hydrochloric acid solution: The concentration is 1:9 by volume ratio of hydrochloric acid to water.

Step: (a). Digestion: Take 0.5 ml of water sample and dilute to 10 ml in a colorimetric tube, and add 5 ml of alkaline potassium persulfate solution. Tighten the lid and tighten the plug with gauze and rubber bands to prevent popping. The colorimetric tube is placed in a high pressure steam sterilizer, heated to the top pressure valve to blow, the valve is closed, and the heating is continued to 120°C, and the temperature is maintained at 120-124°C for 30 min. Naturally cool, open the valve and deflate, take out the colorimetric tube and cool to room temperature, mix. (b). Add 1 ml of hydrochloric acid solution, dilute to 25 ml mark with water, and mix. The formula is as follows:

\[ A = A_{220} - 2A_{275} \]

\[ \rho = \frac{(A-a)x}{fbx} V \text{ (mg/L)} \]
Reagents: (a). Sodium potassium tartrate solution: (500 g/L) 50.0 g of sodium potassium tartrate dissolved in 100 ml of water, heated to boil to remove ammonia, and diluted to 100 ml after cooling.

(b). Nessler reagent: HgI₂-KI-NaOH solution. 16.0gNaOH was weighed into 50 ml of water and cooled to room temperature. Weigh 7.0gKI and 10.0gHgI₂, dissolve in water, slowly add the above NaOH solution in a plate, dilute 100 ml with water, and store in a polyethylene bottle. Store in the dark for 1 year.

Procedure: Dilute 1 ml of water to 25 ml, add 0.5 ml of sodium potassium tartrate solution, add 0.5 ml of Nessler reagent, and shake well. After standing for 10 min, the test was similar at 420 nm, and the blank was the same as above. The calculation formula is as follows:

\[ \rho_N = \frac{(A_c - A_b) - a}{bxV} \text{ mg/L} \]

5. Comparison of carbon source and presence of carrier

In order to compare the practical application effects of two carbon sources, sodium acetate and ethanol, and the effect of adding domesticated carrier and direct dosing compound agent on the system, pre-test 2 was set up. Figures 2 to 5 show that the COD values of the carrier-identified sodium acetate system and the ethanol system both show a significant tendency to decrease with time, and less than 50 mg/L after 4 hours, so that the system is in a low carbon-nitrogen ratio environment. In the system of direct dosing agent, there was no significant difference in COD removal ability from the blank group.

Comparing the carrier nitrification group and the microbial nitrite nitrogen in the direct addition group, the sodium acetate system was slightly better than the ethanol system, and the highest removal effect reached 83.3% in 4h; the comparison carrier domestication group was more effective than the microbial agent. It is much better to directly add the group; however, after 4 hours, the nitrate nitrogen can hardly continue to decline. It is thought that it may be caused by insufficient carbon source in the system, and the COD of the comparative system is known. Since the nitric nitrogen in the blank group is hardly degraded, there is not much accumulation of nitrous oxide. In the direct injection group, the nitrogen and nitrogen decreased a lot after 24 hours of reaction, accompanied by obvious accumulation of nitrous oxide. The nitrous oxide in the acclimated group is also gradually accumulating, and the accumulation in the sodium acetate system is significantly less than in the ethanol system.

The ammonia nitrogen was still detected in this group, and the ammonia nitrogen value produced in the system was almost no, but in a very small interval, it can be seen that the absorbance of the sodium acetate direct injection group is relatively higher, and it may be domesticated with some nitric acid. Salt reduction ammonium.

![Figure 2. Pre-test 2 COD trends](image-url)
6. **Optimization study for temperature and pH**

In order to study whether the subsequent process parameters such as temperature and pH can be optimized, and the total nitrogen removal rate is improved in the ethanol system with low nitrous oxide accumulation, two sets of experiments are set up for different pH conditions and different temperature conditions. The study. And compared with the initial standard conditions of PH = 7.5, temperature = 28°C, the experimental results are shown in Figure 6 to Figure 9.
In a system where the pH is lowered to 6.5, COD can still effectively remove more than 80%, but the removal rate is not satisfactory compared with the removal rate of nitrate nitrogen and total nitrogen, and the removal rate is difficult to reach 50%. The obvious advantage is that nitrous oxide has almost no accumulation. In the system with pH up to 8.5, in addition to COD can still effectively degrade, the trend of other indicators is not optimistic. It is considered that the pH condition is not favorable for the metabolic conditions of denitrifying bacteria. In general, in order to pursue better removal effect, about 7.5 the neutral pH is a good control range.

**Figure 6.** Trend of COD degree under different PH conditions

**Figure 7.** Trend of nitrous oxide content under different pH conditions

**Figure 8.** Trends in nitrate and nitrogen concentrations under different pH conditions
Figure 9. Trend of total nitrogen concentration under different pH conditions

For batch experiments in the temperature group, 24°C and 33°C were added to the initial 28°C system to find an optimized temperature range. The experimental results show that the total nitrogen and COD removal capacity of sodium acetate in the 24°C system is comparable to the 28°C system level, and the nitrous oxide accumulation phenomenon is slightly more obvious, but the overall is better than the ethanol group, and the sodium acetate carbon source group only appears at 33°C. Significant nitrous oxide accumulation. In terms of total nitrogen removal capacity, there is almost no difference between the 33°C and 28°C systems. It is believed that there may be more favorable temperature conditions between them, which remains to be studied, while the total nitrogen removal performance in the 24°C system is not good, COD in multiple systems. The degradation ability is relatively good, and it is obvious that the low carbon and nitrogen micro-pollution conditions are beneficial to the full utilization of organic matter.

Figure 10. Trend of COD concentration under different temperature conditions
Figure 11. Trend of nitrous oxide concentration under different temperature conditions

Figure 12. Trend of nitrate and nitrogen concentration under different temperature conditions

Figure 13. Trend of total nitrogen concentration under different temperature conditions
7. Summary
The experiment takes the carrier FPUFS as the core of the technology and is divided into two parts. The first part is the start of anaerobic reactor, which is mainly used to determine whether the reactor can be started quickly, determine the appropriate range of dosage, compare the difference of water purification effect of adding domestication carrier and direct addition of composite bacteria, and complete microbial domestication. Work and conduct pre-experiments. The second part is the optimization study of process parameters. The effects of different carbon-nitrogen ratios, different pH, different temperature and total nitrogen load on the deep treatment effect of artificially simulated micro-polluted water sources are studied in sequence through static batch experiments.

References
[1] MANTZIARAS I D, KATSIRI A. Reaction rate constants and mean population percentage for nitrifiers in an alternating oxidation ditch system [J]. Bioprocess & Biosystems Engineering, 2016, 34 (1): 57.
[2] SCHMIDT I, HERMELINK C, PASSCHOONEN K V D, et al. Anaerobic Ammonia Oxidation in the Presence of Nitrogen Oxides (NOx) by Two Different Lithotrophs [J]. Applied & Environmental Microbiology, 2012, 68 (11): 5351-5357.
[3] VAN D U, JETTEN M S, van LOOSDRECHT M C. The SHARON-Anammox process for treatment of ammonium rich wastewater [J]. Water Science & Technology A Journal of the International Association on Water Pollution Research, 2011, 44 (1): 153-160.
[4] MUNCH E V, LANT P, KELLER J. Simultaneous nitrification and denitrification in bench-scale sequencing batch reactors [J]. Water Research, 2016, 30 (2): 277-284.
[5] Di Chang, Xia Zhang, Qiong Liu, Ge Gao, Yue Wu. Location based robust audio watermarking algorithm for social TV system. In Pacific-Rim Conference on Multimedia 2012 Dec 4 (pp. 726-738). Springer, Berlin, Heidelberg.
[6] Di Chang, Xia Zhang, Yue Wu. A Multi-Source Steganography for Stereo Audio. Journal of Wuhan University (Natural Science Edition). 2013; 3: 277-284.
[7] Zhang Xia, Chang Di. Sonic audio watermarking algorithm for cable-transmission. The 2rd International Conference on Information Science and Engineering, Vol. 7, 2010, pp. 5395-5398. IEEE Catalog Number: CFP1076H-PRT, ISBN: 978-1-4244-8096-8.
[8] Zhang Xia, Chang Di, Huang Qian. An audio digital watermarking algorithm in DCT domain for air-channel transmitting. Journal of University of Science and Technology of China, Vol (41), 2011.7, pp: 642 – 650
[9] Zhang Xia, Chang Di, Guo Wei, etc. An Audio Steganography Algorithm Based on Air-Channel Transmitting. Journal of Wuhan University (Natural Science Edition), 2011, 57 (6): 499 – 505.
[10] VAN D U, JETTEN M S, van LOOSDRECHT M C. The SHARON-Anammox process for treatment of ammonium rich wastewater [J]. Water Science & Technology A Journal of the International Association on Water Pollution Research, 2011, 44 (1): 153-160.