Shortcut Nitrification and Denitrification in MBBR controlled by Inhibitor

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Abstract. Multi-factor influence on shortcut nitrification in MBBR when dosing methanoic acid-hydrazine\(^2\) was studied in this paper. The results showed that, when the influent ammonia was 30 mg/L and pH was 7.5–8.5, the average nitrite accumulation rate of the reactor without inhibitor (reactor one) and the reactor dosing methanoic acid-hydrazine\(^2\) (reactor two) were respectively 80.2% and 98.5%. When the influent ammonia increased to 50 mg/L, the average nitrite accumulation rate of the reactor one and reactor two were respectively 81.0% and 96.1%. When pH decreased to 6.5–7.0 and other condition unchanged, the average nitrite accumulation rate of reactor one and reactor two were respectively 69.3% and 95.7%. When the pH of the two reactors was 7.5–8.5 and gradually increase the influent ammonia to 300 mg/L, the average nitrite accumulation rate of reactor one and reactor two were respectively 87.7% and 98.3%. When temperature was 12–15 °C, the average nitrite accumulation rate of reactor one and reactor two were respectively 72.4% and 96.9%. From the experimental results, we can see that the realization of shortcut nitrification was the result of multi-factor interaction, the change of each factor affects the realization of shortcut nitrification. However, by adding methanoic acid-hydrazine\(^2\) combined inhibitor in the reactor could reduce the effect on nitrite accumulation when parameters changed in the system and maintain the relatively stable shortcut nitrification.

1. Introduction

Compared with the traditional biological nitrogen remoral process, shortcut nitrification can save oxygen consumption and organic carbon, shortens the hydraulic retention time, and achieve lower sludge production. Shortcut nitrification reduces the cost of wastewater treatment and at the same time makes it possible to efficiently remove nitrogen from wastewater with low carbon to nitrogen ratio[1-2]. There are many factors affecting shortcut nitrification and denitrification, such as pH, DO, temperature, SRT[3-4]. However, in practical application, it is difficult to control nitrite accumulation by single factor control, which increases the difficulty of shortcut nitrification and denitrification. Therefore, in this paper, the effect of adding inhibitors on shortcut nitrification and denitrification was studied.

Other paragraphs are indented (BodytextIndented style). Moving bed biofilm reactors (MBBRs) have been widely applied to treat both urban and industrial wastewaters[5]. MBBRs have significantly lower suspended solids production and can reduce the space compared to traditional activated sludge system, can increase solid retention time for slow growing organisms, and can rapidly recover from extreme loading conditions[6-7].

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Through preliminary experiments, we determined that in SBR the best inhibitor dosage method that control nitrite oxidation is methanoic acid- hydrazine (dosing 0.25 mL/L methanoic acid, every other day dosing 7.5 mg/L hydrazine, and then every other day dosing 7.5 mg/L hydrazine). The objective of this study was to characterize nitrogen removal via nitrite by dosing methanoic acid- hydrazine in the MBBR process, to achieve a stable shortcut nitrification and denitrification attain the purpose of ammonia nitrogen reduction.

2. Materials and Methods

2.1. Configuration of the MBBR

A moving bed biofilm reactor (MBBR) made of organic glass was used for the study shown in figure 1. The peristaltic pump continuously pumps the waste water from the inlet into the bottom of the reactor, and the treated water overflows through the top hole of the reactor. The bottom of the reaction device has a microporous sand core aeration head to ensure sufficient dissolved oxygen and to make the filler fluidized. Aeration is controlled by a rotor flowmeter. The device is provided with partition boards from the bottom aerator head and the top water outlet 5cm to prevent the filler from blocking the sewage outlet and the water outlet. The top cover of the reactor is equipped with adjustable speed mixer, stirring and aeration alternately during operation. By aerobic aeration and anoxic stirring alternately run in the MBBR to better achieve short-cut nitrification and denitrification. The device has a temperature and pH sensor system that automatically regulates the temperature and automatically doses the pH.

Figure 1. Schematic diagram of MBBR

2.2. Synthetic wastewater

Simulated domestic wastewater was used in the experiment. NH4Cl and C6H12O6 were respectively used as nitrogen and carbon source in the synthetic wastewater. The synthetic wastewater also contained NaHCO3 (400mg/L), CaCl2 (4mg/L), KH2PO4 (40mg/L), MgSO4 • 7H2O (40mg/L) and trace elements: FeCl3 (375mg/L), H3BO3 (37.5mg/L), CuSO4 • 5H2O (7.5mg/L), KI (45mg/L), MnSO4 • H2O (25.69mg/L), ZnSO4 • 7H2O (30mg/L), EDTA (2500mg/L), CoCl2 • 6H2O (50mg/L), Na2MoO4 • 2H2O (20mg/L).

2.3. Inoculated sludge characteristics

The inoculated sludge was taken from South Wastewater Treatment Plant (Shenyang, China). Characteristics of inoculated sludge were tabulated in table 1.
Table 1. Characteristics of inoculated sludge

| Parameter | SVI/mL·g⁻¹ | MLSS/mg·L⁻¹ | VSS/mg·L⁻¹ |
|-----------|------------|-------------|-------------|
| Value     | 67.72      | 4430        | 3340        |

2.4. Analytical methods

Samples of influent and effluent were analyzed for selected parameters using qualified instruments and procedures[8]. The analytical methods were shown in table 2.

Table 2. Analytical methods of experimental wastewater quality

| Item       | Method                                           |
|------------|--------------------------------------------------|
| pH         | FE20 pH meter (METTLER TOLEDO, China)            |
| DO         | HQ30d DO meter (HACH Company, USA)               |
| COD        | DR3900 COD meter (HACH Company, USA)            |
| BOD₅       | BODTrakTM (Hach Company, USA)                    |
| NH₄⁺-N     | Nesster's reagent colorimetry                    |
| NO₂⁻-N     | N-(1-naphthyl) ethylenediamine spectrophotometric method |
| NO₃⁻-N     | ultraviolet spectrophotometry                    |
| MLSS       | weight measurement method                        |
| MLVSS      | weight measurement method                        |

3. Results and Comments

3.1. Starting up and acclimation.

The filler used in this experiment was Dalian Yudu (China) modified bio-suspended filler, the filling rate was 50%. The inoculated sludge characteristics were shown in 2.3, and after being acclimated the sludge were put into the reactor to operation. Take the quick discharge method to fill the film and continuous flow biofilm domestication process was conducted using simulate domestic sewage. Two identical reactors (reactor one and reactor two) run at the same time, after nearly 20 days stable operation, the filler in the two reactors has a layer of brown biofilm, then we began to dose methanoic acid – hydrazine² (Dosing methanoic acid first, then dosing hydrazine at the intervals of 24 h and at intervals of 24 h dosing hydrazine again. Repeat the above dosing process at intervals of 24 h) in reactor two.

3.2. Shortcut nitrification and denitrification under the combined action of various factors

The long-term effects of shortcut nitrification and denitrification were studied in the same two reactors by multi-factor synergistic effect. Reactor one did not add inhibitor, reactor two dosing methanoic acid-hydrazine², other operating conditions of the two reactors were the same.

The nitrogen changes of the two reactors during the experiment are shown in figure 2 and figure 3. During the first ten days, pH was 7.5~8.5, the influent ammonia was 30 mg/L. The effluent ammonia of reactor one and reactor two was almost zero, the average nitrite accumulation rate were respectively 80.2% and 98.5%, and the effluent nitrate were respectively 2.85 mg/L and 0.2 mg/L.

From the 11st to the 25th day, the influent ammonia was 50 mg/L, other conditions unchanged. The average effluent ammonia of reactor one and reactor two were all below 1 mg/L, nitrite accumulation rate were respectively 81.0% and 96.1%, and the average effluent nitrate were 4.83 mg/L and 0.96 mg/L respectively. In the past 25 days, the experimental data showed that the ammonia oxidation effect of the two reactors was similar, but the nitrite accumulation rate in reactor two was much larger than that of reactor one, and the effluent nitrate in reactor one was higher than that of reactor two.

The influent pH decreased to 6.5~7.0 in 26~40 days. The average effluent ammonia in the two reactors was still below 1 mg/L, and the average nitrite accumulation rate were 69.3% and 95.7% respectively. The decrease of pH had a great effect on the shortcut nitrification in reactor one, that was
because the suitable pH of the AOB is 7.0~8.5, the suitable pH of the NOB is 6.0~7.5, the decrease of pH destroyed the proper growth environment of the AOB and influence the activity of AOB. On the other hand, the decrease of pH in the system also reduce the FA, and the decreased FA reduced the inhibition of NOB, affecting the accumulation of nitrite. The inhibitory effect of methanoic acid – hydrazine2 on NOB in reactor two filled the inhibition of FA on NOB, so in reactor two could still maintain a higher nitrite accumulation rate.

From the 41st to the 55th day, the pH of the two reactors was 7.5~8.5. Gradually increase the influent ammonia, when the influent ammonia concentration was increased to 300 mg/L and stable operation to measured the experimental results. The oxidation of ammonia was similar in the two reactors, the average effluent ammonia were all below 15 mg/L, and the average nitrate accumulation rate was 87.7% and 98.3% respectively. The nitrite accumulation rate in reactor one increased greatly, the change of nitrite accumulation in reactor two was not great, and the average effluent nitrate of reactor two was 2.21 mg/L, which was slightly increased, but it was far lower than the 18.58 mg/L of reactor two.

The experiment did not control the temperature. However, the experimental data of 1~55 days were measured in summer, the indoor temperature was 25~28°C, and the experimental data of 56~75 days was measured in autumn which indoor temperature was 12~15°C. As can be seen from the figure, during 56~75 days the average effluent ammonia of reactor one and reactor two were 19.69 mg/L and 18.6 mg/L, respectively and the average nitrite accumulation rate were 72.4% and 96.9%, respectively, the data of reactor one fluctuates greatly. The average effluent nitrate were respectively 38.48 mg/L and 3.91mg/L, which were increased compared to the previous experiment. The lower temperature is not suitable for shortcut nitrification, and the temperature decreases result to the FA decreases, which influent the inhibition of NOB.

It can be seen from the experimental data of the two reactors that the realization of shortcut nitrification was the result of multi-factor interaction. The change of each factor affected the realization of shortcut nitrification, but by adding methanoic acid – hydrazine2 could weakened the influence of the parameters in the system on the nitrite accumulation and maintained a relatively stable shortcut nitrification.

![Figure 2. The change of NH₄⁺-N, NO₂⁻-N and NO₃⁻-N in reactor one](image-url)
3.3. Biofacies in the biofilm of the two reactors

The microscopic observations of microorganism in MBBR are shown in figure 4. It can be seen from the pictures that the biofilm flocculus is dense and contains a large number of microbial micelles. In the biofilm microscopic examination of reactor one and reactor two, there were more vorticella, a small amount of suctoria, rotifera, and the aspidisca, which indicating the system was running normally, the biofilm was more active and the wastewater treatment effect was better.
3.4. Scanning electron microscope (SEM) of biofilm
The scanning electron microscope images of the biofilm of reactor one and reactor two are shown in figure 5. It can be seen from the figure that there are filamentous bacteria in the biofilm of the two reactors, which creates favorable conditions for the growth of the microorganisms. The microbes in the biofilm are closely arranged and the microbial biomass in the biofilm of reactor two was more abundant than that in the reactor one.

![SEM images of biofilm](image)

Figure 5. The SEM analysis of the microbial in the biofilm of the reactor

4. Conclusions
In this study, by dosing methanoic acid-hydrazine in MBBR shortcut nitrification and denitrification can be quickly started and long term stable operation of shortcut nitrification and denitrification can be realized. When the operation was stable the biofilm on the filler in the reactor dosing methanoic acid-hydrazine containing a large number of microbial micelles. The SEM images showed that there was exist filamentous bacteria both in the reactor dosing methanoic acid-hydrazine and in the reactor without methanoic acid-hydrazine, and the filamentous bacteria created favorable conditions for the attachment and growth of microorganisms. The microbes in the biofilm were closely arranged and the amount of microbial biomass in the biofilm of the reactor dosing methanoic acid-hydrazine was more abundant than that in the reactor without methanoic acid-hydrazine.

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