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# Effect of low carbon ratio sewage on simultaneous nitrification denitrification and denitrification

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**Abstract.** This test investigated the effect of low C/N ratio wastewater on nitrogen removal in sequencing-batch reactor with continuous aeration of low dissolved oxygen, and evaluated the removal efficiency of nitrogen. The results showed that COD removal was not affected and the removal efficiency was higher than 95% when COD/ $NH_4^+$-N (C/N) was 2.95 and 3.94. The maximum removal rates of the total nitrogen and ammonia nitrogen are 47.4% and 54.7% respectively when C/N is 2.95. The removal rate of the total nitrogen decreases to 13.66% and 16.26% when the C/N reduces to 1.98 and 1.05. The reason for the low removal efficiency of the total nitrogen is that the denitrification reaction is affected by C/N, especially by the lower C/N ratio. In addition, unbalanced nitrification and denitrification reactions lead to low simultaneous nitrification and denitrification efficiency. In the system, the maximum simultaneous nitrification and denitrification efficiency is 94.72%, which occurs when COD/N is 3.94, with very little $NO_x^-$-N in the effluent.

**Key words.** Low C/N ratio, COD removal, Denitrification, Simultaneous nitrification and denitrification.

## 1. Introduction

Wastewater containing excess nitrogen compounds into natural water leads to the eutrophication of water body, seriously affecting the human health and the ecological environment balance and thereby drawing public attention [1]. Nitrogen exists in domestic sewage and industrial wastewater mainly in the form of ammonia nitrogen ($NH_4^+$) and nitrate nitrogen ($NO_3^-$) [2]. Biological nitrogen removal is the most commonly used method, which can be carried out the normal condition without requirement for heating and pressurization in the conversion of pollutants if compared with physical and chemical denitrification, and it is recognized as one of the most promising denitrification methods with simple process, low cost and

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easier promotion as the microorganisms can be acquired fast, propagate rapidly, and has strong environment adaptability [3, 4]. Traditional biological denitrification converts the ammonia nitrogen into nitrite nitrogen and nitrate nitrogen through the nitrification reaction with the aid of nitrifying bacteria, and then converts the nitrite nitrogen and nitrate nitrogen into the nitrogen to be released into the atmosphere by means of denitrifying bacteria to realize the purpose of biological nitrogen removal from sewage [5]. In recent years, with the rapid development in the fields of microbiology and biochemistry, the research and development and application of various new biological denitrification technologies have been promoted. Among them, the synchronous nitrification and denitrification process is one of new denitrification technologies which have been frequently researched. The nitrification and denitrification reactions are allowed to occur in the same operating conditions and within the same reactor, and the simultaneous nitrification and denitrification process has significant advantages over traditional biological denitrification processes, for example, it is capable of effectively maintaining pH stability in the reactor; it consumes a small number of alkali, and the oxygen demand, carbon source consumption and sludge production can be reduced by 25%, 40% and 50%, respectively [6, 7]. Therefore, it draws public attention.

## 2. Test

### 2.1. Test equipment

In this test, the self-made SBR reactor made of plexiglass is used and the reaction operation is controlled by a time-sequencer controller. The reactor has a inner diameter of 100mm, height of 500mm, and effective volume of 3400mL. The bottom of the reactor is equipped with a micro-pore sand-core aeration header. The system is provided with an aeration air source by using an electromagnetic air compressor (Hailea ACO-318), the air pipe is equipped with an air valve which can be used for flow control to adjust the aeration rate, a small submersible pump is placed at the bottom of the reactor if necessary to improve the solid-liquid mixing degree in the reactor, and a drain valve with 20 mm diameter is installed at every 150 mm from the bottom of the SBR reactor wall.

### 2.2. Water quality test

The test water is artificially synthesized, which is mainly composed of NH4Cl, KNO3, KH2PO4, CaCl2, NaHCO3, soluble starch as carbon source, trace elements I (FeSO4) and trace elements II (H3BO3, ZnSO4·7H2O, CoCl2·6H2O, MnCl2·4H2O, CuSO4·5H2O and NiCl2·6H2O).

### 2.3. Analytical method

The main test items in the testing process include: COD, ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, total nitrogen, total phosphorus, SV, PH, MLSS, MLVSS, DO, water temperature and so on. The water quality analysis methods in the test are subject to the fourth edition of "Water and Wastewater Testing and Analysis Methods" prepared by the National Environmental Protection Agency [8].

### 2.4. Test method

This test is designed to investigate the effect of influent with low C/N ratio on nitrogen removal. The concentration of NH3-N in influent is maintained at about 60mg/L, and the COD in influent is changed with adding the starch into the sewage to adjust C/N ratio to 1.05, 1.98, 2.95 and 3.94, respectively. The specific measured values in the test shall prevail. Dissolved oxygen concentration is maintained at about 0.5mg/L, with pH value of 7.5-8.0, and hydraulic retention time of 7h. The influent method is instant water coming-in of limit aeration, with aeration of 7h, precipitation of 1.0h, discharge of treated water in proper order, and the next operation cycle is started after 2h in idle. After the system is stable, the change in the composition of each pollutant in a operation cycle is determined.

## 3. Result and discussion

### 3.1. COD removal

As shown in Fig. 1, there is significant difference in the periodical change of COD concentration in the system, the change trend of COD at C/N ratio of 1.05 is close to that at C/N ratio of 1.98, the change trend of COD at C/N ratio of 2.95 is close to that at C/N ratio of 3.94, the COD removal efficiencies at the said two C/N ratios reach above 95%, indicating that although the COD concentrations in influent are different, they both achieve a high removal rate, and thereby it can be seen that the C/N ratio has no effect on the COD removal. The result is consistent with the conclusions obtained by other researchers [9, 10]. The system has removed 70.30% of COD at a C/N ratio of 3.94 during the first 100 minutes of operation. Until the end of the reaction period, 27% of the remaining COD is removed in 320 minutes. The system with the C/N ratio of 2.95 is not better than the one with the C/N ratio of 3.94 in the removal effect within the short time. However, the COD removal increases from 0 to 63.09% rapidly during the first 140 minutes of operation, and gradually drops subsequently. As shown in the figure, COD removal efficiencies at C/N ratios of 1.05 and 1.98 are much lower than those at C/N ratios of 2.95 and 3.94, with significant fluctuations during system operation. Finally, the removal efficiencies of the two are 57.23% and 70.26% respectively. Analysis on the reasons shows that the rapid reduction of COD concentration in the system at the beginning of the reaction is resulted from the synergy of dilution, the rapid adsorption of activated sludge and the use of microorganism. The organic matter in the sewage is adsorbed to the surface of the microbial cell through the contact with the mud water. Part of the adsorbed organic matter will be hydrolyzed by microorganisms into soluble low-molecular-weight organic matter, and at this point, the COD concentration in the system will rise slightly. With further aeration, the microbial population in the activated sludge gradually enters the endogenous respiration phase, at which point the COD concentration slowly decreases.

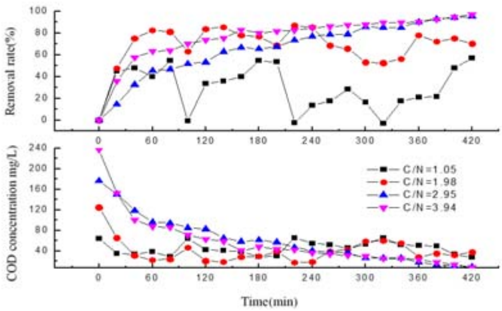


Fig. 1. COD concentration and removal rate during one operation cycle

### *3.2. Removal of ammonia nitrogen and total nitrogen*

The concentrations and removal rates of ammonia nitrogen and total nitrogen in the effluent within reactor at different C/N ratios are shown in Fig. 2 and 3, respectively. Throughout the operation cycle, the removal rates of ammonia nitrogen and total nitrogen are not as ideal as the COD removal efficiency. The removal rates of ammonia nitrogen and total nitrogen with the initial C/N ratio of 2.95 are the highest, as 54.7% and 47.4% respectively, with the effluent concentrations of 27.8mg/L and 32.3mg/L. When the C/N ratio is increased to 3.94, the concentrations of ammonia nitrogen and total nitrogen in effluent are 33.0mg / L and 34.2mg / L at the end of the cycle, indicating that there is a very small amount of $NO_X^-$-N in the system and that almost all of products from the nitrification reaction are denitrified to nitrogen. However, the removal rates are only 41.8% and 39.6%, lower than the results obtained at C/N ratio of 2.95. In general, the removal rates of ammonia nitrogen and total nitrogen at C/N ratios of 2.95 and 3.94 are similar, and the removal rates are 35.9%, 34.5% and 28.0% and 26.3% respectively in the first 60 minutes of the system operation. The ammonia nitrogen and total nitrogen removed within the first 60 minutes of reaction period account for more than 60% of the whole removed, and the remaining part can be removed only 360 minutes has elapsed.

The removal rates of the ammonia nitrogen at the C/N ratio of 1.05 and 1.98 in the influent are 30.6% and 33.4% respectively, and the effluent concentrations are 43.8 mg / L and 39.8 mg / L respectively, with very unsatisfactory effect. There is no obvious fluctuation for the removal of ammonia nitrogen during the whole operation. At the end of the reaction, the total nitrogen concentrations in the effluent at the two ratios reach 52.8 mg / L and 51.6 mg / L, and the removal rates are only 16.3% and 13.7%. Tan and Ng (2007) observed in their study that approximately 15-20% of the concentration of the total nitrogen was removed from the influent by depending on the assimilation of biological cells [11]. Therefore, it is speculated that the removal of total nitrogen in both systems at the C/N ratio of 1.05 and

1.98 is attributed to the assimilation of microorganisms, and a lot of nitrite nitrogen and nitrate nitrogen are accumulated in the system as the denitrification reaction cannot proceed due to the lack of a carbon source and the gradual increase of the DO concentration. In general, no obvious trend that the total nitrogen removal increases with increasing C/N ratio is observed in this test. However, four different C/N ratios show significant similarity in pairs with obvious difference in terms of total nitrogen removal. At the same time, the total nitrogen removal also indicates that there is denitrification phenomenon in the reactor under continuous aeration, that is, synchronous nitrification and denitrification reactions occur.

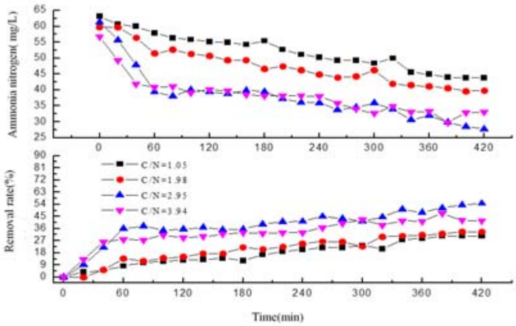


Fig. 2. $NH_4^+$-N concentration and removal rate during one operation cycle

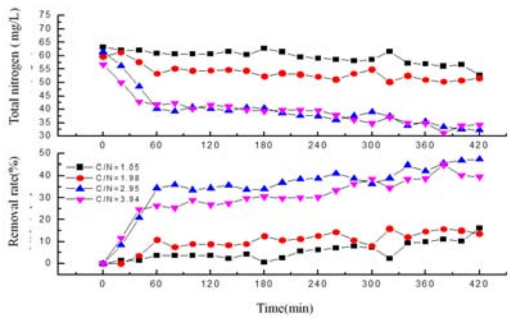


Fig. 3. TN Concentration and removal rate during one operation cycle

### *3.3. Effect of influent at low C/N ratio on the nitrification and denitrification reaction*

The rates of nitrification and denitrification reactions in the system are calculated according to equations (1) and (2). Equation (3) is used to calculate the efficiency of simultaneous nitrification and denitrification reactions, which was proposed by Katie et al. in 2003 [12]. All the statistics are summarized in Tab. 1.

$$\text{rnitrification} = \frac{Q_{\text{in}}(\text{NH}_4^+ - N_{\text{influent}} - \text{NH}_4^+ - N_{\text{effluent}})}{V_{\text{reactor}}} \tag{1}$$

$$\text{rdenitrification} = \frac{Q_{\text{in}}(\text{TN}_{\text{influent}} - \text{TN}_{\text{effluent}})}{V_{\text{reactor}}} \quad (2)$$

$$\text{EfficiencySND} = (1 - \frac{\text{NO}^-_{x\ \text{remained}}}{\text{NH}^+_{4\ \text{oxidized}}})100 \quad (3)$$

Qin represents the influent flow (L / h), Vreactor refers to the reactor volume (L); $NO_x^-$ is the remaining $NO_x^-$ after the end of the reaction, and $NH^-_{4\ \text{remained}}$ means the oxidized $NH_4^+$ after the end of the reaction.

It can be seen from Tab.1 that the nitrification reaction rate is generally better than the denitrification reaction rate, in which the nitrification reaction rate at the C/N ratio of 2.95 is the maximum, with the value of 16.00mg / (L h), while the other three had little difference, indicating that the C/N ratio does not have a significant effect on nitrification reaction rate and proving that the nitrification reaction dominated by autotrophic bacteria is the main reaction in the system at low C/N ratio [13]. The denitrification reaction rates at the C/N ratios of 2.95 and 3.94 are much higher than those at the C/N ratios of 1.05 and 1.98, and the denitrification reaction rate increases significantly with increasing the C/N ratio, indicating that the C/N ratio has a significant effect on denitrification reaction rate probably due to the need for an organic carbon source as an electron donor. The denitrifying bacteria uses carbon sources successively. Firstly, the easily degradable organic matters such as volatile fatty acids are utilized, which are followed by the organic matter difficult to be degraded in the system. Finally, the carbon source stored in the cell is used. The denitrification reaction rate depends on the carbon source utilized and decreases in this order.

Many researchers believe that efficient simultaneous nitrification and denitrification occurs when the nitrification and denitrification reaction rates are in equilibrium and there are fewer nitrite nitrogen and nitrate nitrogen produced in the system [14, 15]. Therefore, the system under test conditions with influent C/N ratios of 2.95 and 3.94 results in more efficient simultaneous nitrification and denitrification efficiencies of 86.56% and 94.72% respectively, which is consistent with the calculated results in Table 1.

Chiu et al. concluded from their study that the simultaneous nitrification and denitrification efficiencies reach 98.7% and 97.1% at C/N ratios of 11.1 and 19.7, respectively [9]. At the initial C/N ratio of 14.5, Pochana and Keller obtained about 80% simultaneous nitrification and denitrification rates [16]. In summary, an efficient simultaneous nitrification and denitrification system requires not only balanced nitrification and denitrification reactions but also high nitrification and denitrification rates.

Table 1. The SND efficiencies and nitrification and denitrification rates with low C/N ratios

| C/N ratio | rnitrification(mg/L·h) | rdenitrification(mg/L·h) | Efficiency of SND% |
|---|---|---|---|
| 1.05 | 9.18 | 4.88 | 53.19 |
| 1.98 | 9.49 | 3.88 | 40.84 |
| 2.95 | 16.00 | 13.85 | 86.56 |
| 3.94 | 11.29 | 10.69 | 94.72 |

## 4. Conclusion

In terms of COD removal, the system with influent C/N ratios of 2.95 and 3.94 is not affected, and the removal efficiencies of both are over 95%. When the C/N ratio is reduced to 1.05 and 1.98, COD removal is significantly affected, with substantial fluctuations during the system operation, and finally, the removal rates are 57.23% and 70.26%.

The nitrification reaction rate is generally better than the denitrification reaction rate, proving that the nitrification reaction is the main reaction in the system at low C/N ratio and that the effect of C/N ratio is not significant.

The influent with Low C/N ratio has a great influence on denitrification reaction rate which sharply increases with the increase of C/N ratio, and the denitrification reaction rates at the C/N ratios of 2.95 and 3.94 are much higher than those at the C/N ratios of 1.05 and 1.98. The fluctuation of the denitrification reaction rate leads to the imbalance it and the nitrification reaction rate, thus reducing the efficiency of the simultaneous nitrification and denitrification. The efficiency of simultaneous nitrification and denitrification with C/N ratio of 3.94 is the maximum in the test, which is 94.72% and followed by 86.56%, the efficiency of simultaneous nitrification and denitrification with C/N ratio of 2.95.

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