The influence of alkalinity on the two stages of S0-based autotrophic denitrification

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Abstract. In this study, two S0 particle packed reactors were constructed to explore the influence of alkalinity content on S0-based autotrophic denitrification (SAD) with nitrate and nitrite as electron acceptors respectively. As a result of the comparative experiment, when the alkalinity of influent is sufficient (HCO3: NO3 mole ratio ≥ 1.5:1), NO3--N and NO2--N reactor both showed high removal efficiency. But when the HCO3: NO3 mole ratio decreased to 0.2:1, the average removal rate of NO3--N decreased to 31%, and NO2--N average removal rate still maintained at 95%. Based on the results, the reduction of alkalinity can significantly reduce the nitrate removal efficiency, but has little effect on the nitrite removal efficiency. This study further explained the characteristics of alkalinity consumption of the two stage of SAD and may provide a reference for future research.

1. Introduction

Nitrogen pollution is one of the main problems in water environment, and also one of the main factors causing eutrophication of water body. The effluent from wastewater treatment plant is one of the main sources of nitrogen pollutants in water environment system, and nitrate is the main component of nitrogen pollutants. Therefore, the removal of nitrate in wastewater treatment plant is very important for the improvement of water environment quality.

Heterotrophic denitrification is the main technology for nitrate removal in wastewater treatment, but its effect is affected by the content of organic carbon, especially the wastewater with low C/N ratio need to add methanol, ethanol and acetate, etc. as electron donors [1]. It often has problems of expensive cost, overdoing concern and high sludge yields. Autotrophic denitrification use inorganic matter (such as S0, S2-, S2O32-, SO32-, H2, Fe2-) as electron donor instead of organic matter to reduce the nitrate to nitrogen can effectively solve this problem [2, 3]. Elemental sulfur (S0) based autotrophic denitrification is favored because it is nontoxic, odorless, and does not have excessive dosage problems as a solid. SAD was usually used in the form of fixed bed for nitrogen removal of low-carbon industrial wastewater and deep denitrification treatment of tail water in municipal sewage treatment plant. The stoichiometry of SAD is as shown in the following equation [4]:

\[ NO_3^- + 1.1S^0 + 0.4CO_2 + 0.76H_2 + 0.08NH_4^+ \rightarrow 0.5N_2 + 1.1SO_4^{2-} + 1.28H^+ + 0.08C_5H_7O_2N \]  

(1)

It can be seen from the above that removal of 1mol NO3- will produce 1.28mol H+, which means that the process requires a lot of alkalinity. It is also expensive. To solve this problem, limestone was usually
used to provide alkalinity mixed with S\textsuperscript{0} particle in packed bed reactor, because of its low cost and availability \cite{5, 6}. However, the addition of limestone occupied a part of the reactor volume, which reduced the denitrification efficiency. In addition, the dissolution of limestone would lead to an increase in the concentration of calcium ions, resulted in scaling of the tank walls and pipes. In view of this, some studies constructed the mixotrophic denitrification system by adding amount of organic carbon source such as liquid organic matter, wood-chip and corn core in the SAD system to reduce alkalinity consumption and sulfate production \cite{7, 8, 9}. In the mixed system of autotrophic and heterotrophic denitrification, no matter what form of organic carbon source was added, the biomass yield would be higher than that of the elemental sulfur autotrophic denitrification system alone. At the same time, it might lead to the conversion of sulfate to hydrogen sulfide gas under anaerobic environment, causing the odor problem due to the existence of organic matter. SAD process consists of two stages, nitrate is first reduced to nitrite, and then reduced to nitrogen \cite{10}. These studies usually focused on the overall effect of the system and the microbial composition and rarely studied the alkalinity consumption characteristics of the two stages of the SAD separately.

In this study, we constructed two S\textsuperscript{0} particle packed reactor to explore the influence of alkalinity dosage on the two stages of denitrification process respectively. The results can further explain the characteristics of alkalinity consumption and provide a reference for future research.

![Fig. 1. The experimental device of SAD used in the present study](image)

2. Materials and methods

2.1 Set-up of SAD reactor

The experimental set-up of SAD is shown in Fig.1. Two continuous upflow fixed bed cylindrical reactors (R1, R2) packed with 3-5mm diameter elemental sulfur particles were used in this study. The effective volume of the reactor was 1L with 50mm diameter and 500mm high. Each reactor was inoculated with 100mL activated sludge from a municipal sewage treatment plant at a concentration of about 3500 mg/L, and the empty bed contact time (EBCT) was set to 1h. The reactor was operated at room temperature (24~28\textdegree C) without additional insulation. 5 sampling points were uniformly set along the direction of height on two reactors.

2.2 Wastewater composition

Artificial synthetic wastewater was used in this study, which was composed of NO\textsubscript{3}⁻-N (R1, 50mg/L) and NO\textsubscript{2}⁻-N (R2, 50mg/L), 13mg/L KH\textsubscript{2}PO\textsubscript{4}, 10mg/L MgSO\textsubscript{4}·7H\textsubscript{2}O, 5mg/L CaCl\textsubscript{2}·2H\textsubscript{2}O, 0.5mL/L trace element 1, and 1mL/L trace element 2, where trace element solution 1 contained (g/L): EDTA-2Na 6.37, FeSO\textsubscript{4}·7H\textsubscript{2}O 9.15; trace element solution 2 contained (g/L) EDTA-2Na 19.11, ZnSO\textsubscript{4}·7H\textsubscript{2}O 0.43, CoCl\textsubscript{2}·6H\textsubscript{2}O 0.24, MnCl\textsubscript{2}·4H\textsubscript{2}O 0.99, CuSO\textsubscript{4}·5H\textsubscript{2}O 0.25, NaMoO\textsubscript{4}·2H\textsubscript{2}O 0.22, NiCl\textsubscript{2}·6H\textsubscript{2}O 0.19, NaSeO\textsubscript{4}·10H\textsubscript{2}O 0.21, H\textsubscript{3}BO\textsubscript{4} 0.014. Alkalinity in influent was provided by NaHCO\textsubscript{3}, whose concentration changes for different operating periods is listed in Table 1.
Table 1. NaHCO₃ concentration in influent

| Time (d) | HCO₃⁻: NO₃⁻ (mole ratio) | NaHCO₃ (mg/L) |
|----------|--------------------------|--------------|
|          | R1 | R2         | R1 | R2         |
| 0~24     | 1.5:1 | 450 | 450 | 450 |
| 25~44    | 1.0:1 | 300 | 300 | 300 |
| 45~60    | 0.5:1 | 150 | 150 | 150 |
| 61~78    | 0.2:1 | 60  | 60  | 60  |
| 79~100   | 1.5:1 | 450 | 450 | 450 |

2.3 Analytical methods
The NO₃⁻-N (Ultraviolet spectrophotometry method, HITACHI U-5100) and NO₂⁻-N (Ultraviolet spectrophotometry method, HITACHI U-5100) concentrations in the influent and effluent were measured every two days. SO₄²⁻ was measured using ion chromatography method (Thermo Fisher AQ-1100), and pH was measured using pH meter (METTLER, S2). In addition, samples along the reactor were obtained three times through the sampling point on the reactor at 79~100d.

3. Results and discussion

3.1 The influence of alkalinity on SAD with nitrate as electron acceptor
In Fig.1, NO₃⁻-N removal effect decreases significantly when the alkalinity of influent decreases. The initial average NO₃⁻-N removal rate is 90% when HCO₃⁻: NO₃⁻ mole ratio in influent is 1.5:1. Then as the HCO₃⁻: NO₃⁻ mole ratio decreases to 0.2:1, average removal rate of NO₃⁻-N decreases to 31%. However, it is worth noting that the nitrate removal rate recovered immediately when HCO₃⁻: NO₃⁻ mole ratio is increased from 0.2:1 to 1.5:1 straightly again. The decrease in alkalinity of influent does not result in significant accumulation of nitrite, except during the initial start-up of reactor. It can be seen that in the process of nitrate reduction, whether the alkalinity is excessive or not may not cause the accumulation of nitrite. And the complete removal of nitrate of reactor requires a minimum HCO₃⁻: NO₃⁻ mole ratio of 1.5:1 in influent.

2.3 Analytical methods

2.3.1. The influence of alkalinity on SAD with nitrate as electron acceptor

3.2 The influence of alkalinity on SAD with nitrite as electron acceptor
The relationship between the removal effect of NO₂⁻-N and the change of alkalinity in influent is shown in Fig.2. It can be seen that the reduction of alkalinity in influent within a certain range has little effect on NO₂⁻-N removal effect. When the mole ratios of HCO₃⁻: NO₃⁻ are 1.5:1 and 1:1, NO₂⁻-N removal rate reaches to nearly 100%. Although the removal effect of NO₂⁻-N has a slight reduction as the HCO₃⁻: NO₃⁻ mole ratio decreases to 0.5:1 and 0.2:1, there is still an average removal rate of 92%. The nitrite
removal rate recovers to almost 100% immediately when HCO$_3^-$: NO$_3^-$ mole ratio increases from 0.2:1 to 1.5:1 straightly. During the whole operation, the lowest nitrite removal rate is 83% occurs when HCO$_3^-$: NO$_3^-$ mole ratio changes from 0.5:1 to 0.2:1, and then increases rapidly. It can also be seen that complete removal of nitrite requires little or no alkalinity as long as the appropriate pH is maintained.

Fig. 3. Nitrite concentration of R2 (SAD with nitrite as electron acceptor)

### 3.3 The characteristics of SAD process with excess alkalinity

When the HCO$_3^-$: NO$_3^-$ mole ratio in influent is 1.5:1, the concentrations of nitrate, nitrite and sulfate change along R1 is shown in Fig. 4. Nitrate content decreases gradually with the increase of time along the reactor, while the sulfate concentration increases. The mass ratio of SO$_4^{2-}$-S increment to NO$_3^-$-N decrement is 1.94 nearly to the theoretical value. Only a small amount of nitrite appears at the first sampling point in the entire reactor and then reduces to nearly zero. And it also can be seen that the reaction rate of nitrate decreases with the increase of reactor height, which may be reasons for the decrease of substrate concentration, alkalinity and pH [11]. And Nitrate is mainly removed in the first 40 minutes of the reactor, and the removal rate is about 90%.

Fig. 4. Changes of nitrate, nitrite and sulfate concentration along the reactor1 (R1)

Fig.5 shows the concentrations of nitrite and sulfate change in R2 when influent HCO$_3^-$: NO$_3^-$ mole ratio is 1.5:1. With the increase of contact time in the reactor, nitrite decreases gradually and sulfate increases gradually, and mass ratio of SO$_4^{2-}$-S increase to NO$_2^-$-N decrease is 1.18 nearly to the theoretical value. It’s worth noting that the reduction rate of NO$_2^-$-N in the first half reactor is much higher than in the second half, so that 95% nitrite was removed in the first half an hour.
Combined with the results of Fig. 4 and Fig. 5, it can be seen that the removal rate of nitrite of R2 is significantly higher than that of nitrate in R1. And removing the same amount of NO$_3^-$-N produces 1.6 times as much sulfate as removing the same amount of NO$_2^-$-N by comparing two reactors.

4. Conclusions
The effect of alkalinity content in influent on the two stages of SAD is very different. The reduction of alkalinity can significantly reduce the nitrate removal efficiency, but has little effect on the nitrite removal efficiency. When the HCO$_3^-$: NO$_3^-$ mole ratio decreases to 0.2:1, the average removal rate of NO$_3^-$-N decreases to 31%, but the average removal rate of NO$_2^-$-N can still maintain at 95%. And the decrease of alkalinity may also reduce the reaction rate significantly.

Acknowledgements
This work was supported by Shenzhen Science and Technology Innovation Commission (Grant number JCYJ20180306172051662, KQJSCX20180328165658476, JCYJ20200109113006046, KCXFZ20201221173602008 and KCXFZ202002011006362).

References
[1] HAN F, ZHANG M, SHANG H, et al. Bioresource Technol 315, 123826 (2020)
[2] DI CAPUA F, PIROZZI F, LENS P N L, et al. Chem. Eng. J 362, 922-937 (2019)
[3] LIN S, MACKAY H R, HAO T, et al. Water Res 143, 399-415 (2018)
[4] WANG Y, BOTT C, NERENBERG R. Water Res 100, 184-193 (2016)
[5] LY Y, WANG Y, WAN D, et al. Bioresource Technol 300, 122682 (2020)
[6] LIANG J, CHEN N, TONG S, et al. Chemosphere 212, 954-963 (2018)
[7] QIU Y, ZHANG L, MU X, et al. Water Res 169, 115084 (2020)
[8] ZHANG R, XU X, CHEN C, et al. Water Res 143, 355-366 (2018)
[9] LI R, FENG C, HU W, et al. Water Res 89, 171-179 (2016)
[10] KOSTRTYTSIA A, PAPIRO S, MATTEI M R, et al. Water Sci. Technol 78 (6), 1296-1303 (2018)
[11] HUANG S, ZHENG Z, WEI Q, et al. Bioresource Technol 194, 122176 (2019)