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Mechanism of Rapid Reaction of Sulfate Type Anammox by Different Acid and Alkali Value Environment

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Sulfate itself is not toxic, but it is easily reduced by sulfate reducing bacteria (SRB) to hydrogen sulfide (H_2S) gas under anaerobic conditions. H_2S can seriously corrode the drainage pipeline and some water treatment facilities, and make water body black hair odor pollution of the water environment. In addition, H_2S odour and odour, when reaching a certain concentration, can cause human neurotoxicity, and react with ozone in the atmosphere to form sulfuric acid to form acid rain. This paper is mainly to study the mechanism of rapid reaction of sulfate type anammox by different acid and alkali value environment.

1. Introduction

With the continuous improvement of the living standards of the people and the rapid development of industry and agriculture, the discharge of waste water has also increased. In many industries, it contains not only high concentration of ammonia nitrogen, but also high concentration of sulphate (Rattray et al., 2008). The emission of high ammonia nitrogen will reduce the dissolved oxygen of the water body rapidly, and lead to the eutrophication of the water body (Bae et al., 2007). If the treatment is not complete enough, ammonia can also be transformed into a "three" substance, which is a serious threat to human health (Rikmann et al., 2014). The waste water containing ammonia nitrogen and sulfate cannot reach the standard discharge, which not only causes the excess of ammonia nitrogen and sulphate in the surface water, but also pollute a lot of groundwater (Ahn et al., 2004). Therefore, how to deal with high ammonia nitrogen and sulfate wastewater steadily and efficiently is a greater challenge to the technology of wastewater treatment (Okamoto et al., 2013).

The removal of nitrogen containing wastewater is mainly based on the traditional nitrification denitrification organisms, that is, by means of nitrifying bacteria and denitrifying bacteria, ammonia nitrogen is converted to nitrate nitrogen under aerobic and anoxic environment, and then nitrate nitrogen is reduced to organic nitrogen. For the wastewater containing sulphate, it is generally removed from the waste water by the effect of anaerobic desulfurizing bacteria (Kawagoshi et al., 2010). This step by step removal method not only increases engineering investment and operation cost, but also makes processing technology more complex and poor operation stability, which brings great difficulty to operation management. In contrast, the process of synchronous denitrification and desulfurization of wastewater has effectively solved these problems.

2. Reaction mechanism of sulfate - type oxyammonia oxidation

It is found that the oxidative ammonia oxidation can be carried out under the condition of organic carbon source and inorganic carbon source (Liang et al., 2009). This provides a variety of conditions for the realization of simultaneous denitrification and desulfurization in wastewater treatment (Yao et al., 2015). However, it is necessary to study the reaction mechanism from the reaction mechanism in order to understand the process of sulfate oxidation reaction (Zhan and Zhang, 2018).

2.1 Stoichiometry

The theory of stoichiometry is one of the bases of material balance and heat balance in the reaction process. This theory investigates the transmission or change of various factors in the reaction system (reaction substrate type, concentration, alkalinity, etc.), and the mechanism of reaction is clear. Fdz-polanco et al.

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proposed the mechanism of the oxidation reaction of sulfates in the organic carbon source, and the study found that 50% of the total nitrogen converted N_2. About 60% of SO_4^2 is converted to sulfur, and the reaction equation is.

$$3SO_4^{2-} + 4NH_4 \rightarrow 3S^{2-} + 4NO_2^- + 4H_2O + 8H^- \quad (1)$$

$$3S^{2-} + 2NO_2^- + 8H^- \rightarrow N_2 + 3S + 4H_2O \quad (2)$$

$$2NH_4^- + 2NO_2^- \rightarrow 2N_2 + 4H_2O \quad (3)$$

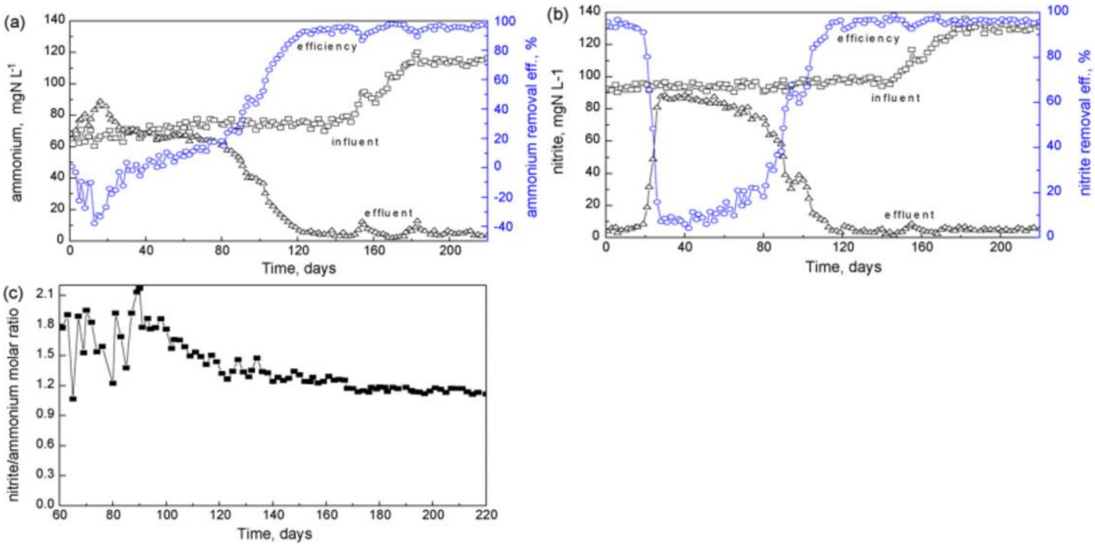

Figure 1: Influent and effluent ammonium and nitrite concentrations, efficiencies and ratio

From the above equation, it can be seen that the sulfate type oxyammonia oxidation is a step reaction. First, SO_4^2 and NH_4^+ generate NO_2^- and S^{2-}. And then S^{2-} and partial NO_2^- react to generate N_2 and elemental sulfur, and finally NH_4^+ reacts with the remaining NO_2^- to produce N_2. The loss ratio of nitrogen to sulfur is 2. However, we believe that at least 50% of NH4+ -n is converted to N_2 and 88% of SO_4^{2-} converted to elemental sulfur, so the loss ratio of nitrogen sulfur is 0.81. We obtained from the experiment that the conversion amount of NH4+ -n is higher than that of SO_4^{2-} and the ratio is much higher than 2. The nitrogen sulfur loss ratio determines the amount of the reaction matrix and the relationship between the product and the reactant. Although the researchers obtained different nitrogen and sulfur loss ratios, the production of S^2-, HS- and elemental sulfur was found in the study, so the reaction equation proposed by the authors was more favourable. In addition, we think is not suitable for sulfur nitrogen than the water can make the S^{2-} sulfur autotrophic denitrification and regenerate the SO_4^{2-} and appeared in the product, when will fill sulfur nitrogen ratio regulation 0.75, reaction products in the elemental sulfur SO_4^{2-}, and detection in the product to a small number of intermediate hydrazine and hydroxylamine, reaction equations are as follows:

$$3S^{2-} + 4NO_2^- + 4H_2O \rightarrow SO_4^{2-} + 2S + 2N_2 + 8OH^- \quad (4)$$

Under anaerobic conditions, organic carbon sources can provide substrates for sulfate reducing bacteria, promote sulfate reduction, and reduce SO_4^{2-} to HS^- or S^{2-}. This process will also affect sulfate oxidation. Sulfate reducing bacteria not only have fast growth rate, but also contain unoxygen toxic enzymes, which guarantee the stronger viability of sulfate reducing bacteria. Therefore, under a certain carbon source, the sulfate type oxygen ammonia oxidizing bacteria can symbiotic with the sulfate reducing bacteria, but the sulfate reducing bacteria are more capable of reacting. The results show that low COD, high NH4+ and alkaline conditions are beneficial to the reaction of Kraft oxygen and ammonia oxidation. We also think that high COD is beneficial to desulphurization, but it inhibits the Kraft oxygen ammonia oxidation reaction. Under the condition of inorganic carbon source, no generation of S^{2-} was detected during start-up. They thought that although the simultaneous removal of nitrogen and sulfur occurred, there were different reaction mechanisms with organic carbon sources. By calculating the conservation of material, the following reaction equation is proposed.

$$SO_4^{2-} + NH_4^- \rightarrow NO_2^- + S + 2H_2O \quad (5)$$

$$2NO_2^- + 2NH_4^- \rightarrow 2N_2 + 4H_2O \quad (6)$$

As a result, the consumption of 1 mole of SO_4^{2-} needs to consume 3 mole of NH_4^+, and the consumption of 1 mole of NO_2^-, and the alkalinity of the reaction process. However, our results show that there are N_2, elemental sulfur and NO_3^- in the product, but the production of NO_2^- is not observed, so the above reaction is not reasonable. When we start the Kraft oxygen ammonia oxidation reaction, it is also found that NO_3^- is produced and the maximum amount of production is up to 77.6mg/L, so the reaction equation is improved as follows:

$$SO_4^{2-} + NH_4^- \rightarrow NO_2^- + S + 2H_2O \quad (7)$$

$$4SO_4^{2-} + 3NH_4^- + 2HCO_3^- \rightarrow 4S + 3NO_3^- + 7H_2O + 2CO_3^{2-} \quad (8)$$

$$2NO_2^- + 2NH_4^- \rightarrow 2N_2 + 4H_2O \quad (9)$$

Due to the gradual replacement of NO2- by SO42- instead of NO2-, the sulfate oxidation of ammonia is initiated. The traditional anammox process is not enough to generate such a large amount of NO3-, which should be generated by other ways. From the reaction mode, the production of NO2- or NO3- is related to the ratio of nitrogen to sulfur. When nitrogen and sulfur are relatively low, NH4+ can provide enough electrons to restore SO42- by over oxidation to NO3-, thereby improving the conversion rate of SO42- and the generation rate of NO3-. At the same time, it is also related to the Gibbs free energy of the reaction, and the lower Gibbs free energy is beneficial to the reaction. We think the reaction of sulfate type oxygen and ammonia oxidation is a process of decreasing p H. The process of producing NO3- by the redox reaction of SO42- and NH4+ is the decline of P H, which can explain the decline of P H in the whole system. To sum up, the reaction mechanism of sulfate type oxygen ammonia oxidation is not clear. Each research team has different views on the changes of the matrix, product and P H of the reaction. Because the reaction start time is longer, the research is less, so how to control the conditions to make the reaction more rapid start is the first problem to be solved.

2.2 Microbiology theory

The theory of microbiology is to study the basic rules of life activities such as the morphological structure, growth and reproduction, physiological metabolism and other life activities of all kinds of micro-organisms at the level of molecules, cells or groups. Sulfates can survive in inorganic carbon source conditions, indicating that sulfates are autotrophic bacteria. The growth rate of bacterial species is slow, and the growth rate of p H is alkaline, the optimal growth temperature is about 35 degrees, and the dissolved oxygen is less than 0.5 mg/L, which belongs to anaerobic bacteria. It is believed that low REDOX potential is beneficial to the growth of this species. At present, has been less clear sulfate type strains of anaerobic ammonia oxidation, we used the PCR - DGGE respectively of MBBR (moving bed biofilm reactor) within the biofilm and UASB (up flow anaerobic sludge bed), the observation analysis of sludge reactor microbes found belong to Planctomycetales and Verrucomicrobia door respectively. We analysed the microbial population in the bioreactor reactor by pcr-dgge and 16Sr DNA technology, and believed that there existed a dominant species of Anam moxylbus sulfate. We of the sludge in the reactor through scanning electron microscopy observation, found that the sludge mainly chain bacillus and staphylococcus aureus, its size, respectively (1 ~ 1.2) μm x 0.8 μm and 0.8 μm, transmission electron microscopy show that bacterial cells contain a large amount of inclusions. The authors used pcr-dgge to analyze the changes of microorganism from traditional anaerobic ammonia oxidation to sulfate-anaerobic ammonia oxidation. The authors found that the bacteria in the sludge changed from micrococcus to short bacillus, and the length was about 2~3 mu m. Bacillus benzoevorans were the dominant species of bacteria in the bacterial flora, which was the dominant species, indicating that the two anaerobic ammonia oxidation were not the same bacteria. Research, we found that the Bacillus can be without the presence of oxygen molecule state, sulfate as electron acceptor oxidation of ammonia and sulfate type anaerobic ammonia oxidation ability, sulfate type anaerobic ammonia oxidation phenomenon is likely to be caused by the Bacillus reproduction. The distribution of sulfates is widely distributed, and it has been successfully selected from anaerobic sludge, river sediment, denitrification sludge and traditional anaerobic ammonia sludge. Usually think, sulfate type anaerobic ammonia oxidation bacteria can survive in organic carbon source, but if we can use the presence of organic matter and organic compounds can inhibit the activity of sulfate type anaerobic ammonia oxidation bacteria is unknown. However, it is believed that low concentration of organic matter can guarantee the oxidation of sulfates.

3. Denitrifying nitrogen removal and desulfurization

The principle of denitrifying denitrification and desulfurization is that, under anaerobic conditions, denitrifying desulfurization bacteria can oxidize sulfide to SO_4^{2-} or simple S biological reaction process with NO_3^- or NO_2^- as electron acceptor. For the treatment of waste water containing ammonia and sulfate, if you want to achieve the purpose of the removal of ammonia nitrogen and sulphate at the same time, need to be under the action of sulfate reducing bacteria (SRB), sulfate reduction into sulfide (including H_2S, S^{2-} and HS -). Ammonia nitrogen was oxidized to nitrate under aerobic conditions, so that the denitrification and desulfurization and desulfurization reaction could occur under certain conditions. The anti-nitrifying bacteria of strict self-cultivation can only be used as electron donor for the original sulfur compound, and the inorganic carbon is the carbon source, and NO_3^- is reduced to N_2. In addition, it can be used to raise anti-nitrifying bacteria, which can take advantage of the original sulfur compounds and organic carbon compounds. Based on two different denitrifying autotrophic bacteria, a variety of simultaneous denitrification and desulfurization technologies emerged.

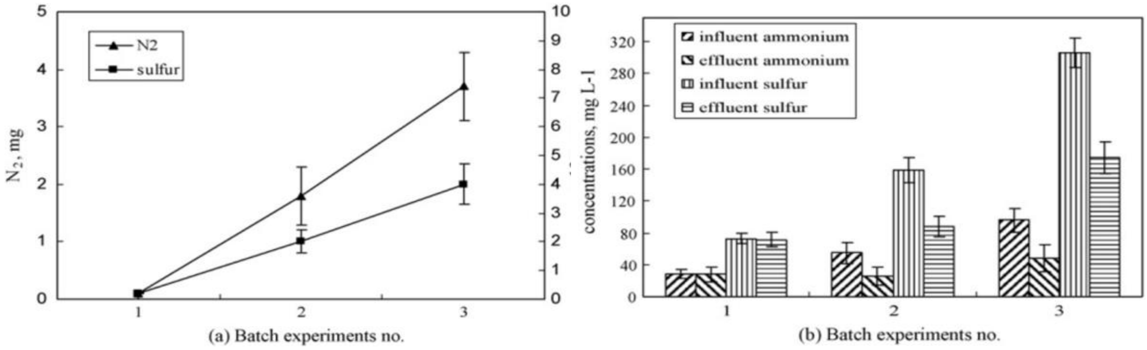

Figure 2: Batch tests in various concentration of ammonium and sulfate

3.1 Autotrophic denitrification desulphurization

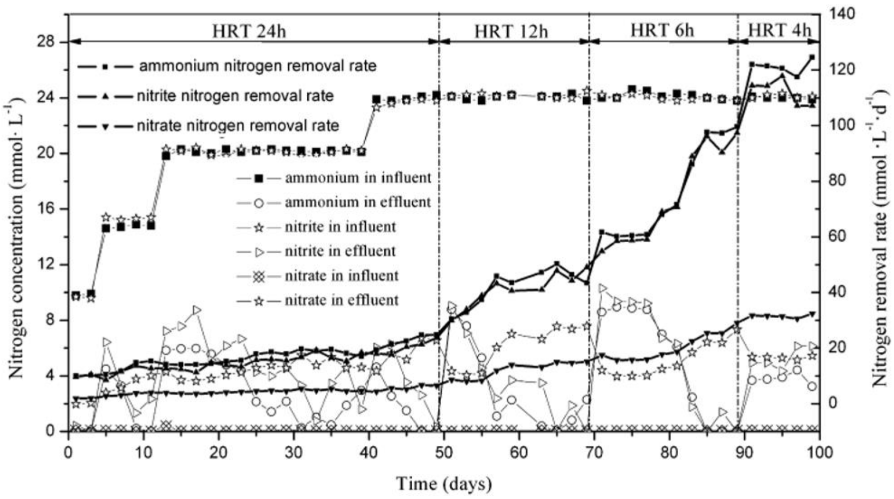

Figure 3: Time courses of ammonium removal rate, nitrite removal rate and nitrate production rate during the operation of anammox process

We found that the sulfur nitrogen ratio was regulated at a higher level, which could improve the selectivity of the anaerobic biosynchronous denitrification and desulfurization reaction on the elemental sulfur and nitrogen. Under the condition that the sulphide concentration was 520 mg/L and the sulfur nitrogen ratio was 5/2, 5/5 and 5/8 respectively, the corresponding sulfate yield was 8.6%, 14.7% and 36.6% respectively. The actual sulfate yield is lower than the theoretical calculation, the main reason is that the nitrate cannot be completely reduced to nitrogen, and the effect is enhanced with the increase of the substrate concentration.

Although some progress has been made in the study of self-feeding denitrification and sulfur oxidation technology, there are still obvious disadvantages in application. In the process, there is a large amount of sulfates in the water to cause the secondary pollution of the environment, and the operation cost of the process is increased by adding the elemental sulfur and limestone. Normally, strictly autotrophic denitrifying bacteria can only use inorganic carbon as the carbon source, and the original sulfur compound as the electron donor, and the organic matter has the inhibitory effect on its degradation activity. Wastewater often contains a certain concentration of organic carbon compounds, and the application of autotrophic denitrification in the desulfurization of wastewater is limited.

3.2 Hybrid denitrification technology

Some researchers used the combination of non-strict self-supporting denitrifying bacteria and heterotrophic denitrification to achieve the simultaneous removal of nitrogen, sulfur and organic carbon, namely, the process of mixed oxygen denitrification.

For the first time, we adopted the technology of simultaneous removal of carbon nitrogen and sulfur under mixed nutrition. They used fluidized bed reactor for small test, which realized the simultaneous removal of sulfide, organic carbon and nitrate, but the conversion rate of sulfide into elemental sulfur was extremely low, only 0.3%. We used a CSTR reactor with a working volume of 1.3L to conduct denitrification removal of carbon and nitrogen sulfur under HRT=2d conditions. It is clear how the sulfide and acetic acid are metabolized under the condition of denitrification, and the changes of the three channels meet the following rules: Nitrate reduction rate of nitrite> the rate of nitrate reduction to nitrite under the action of acetate> the elemental sulfur denitrifies the nitrite to the rate of harmless nitrogen.

In order to solve the problem of low sulfur conversion rate in the process of process, we first proposed the new idea of simultaneous denitrification and desulfurization process with the goal of recovery of elemental sulfur. By controlling the process operating conditions, especially sulfur, nitrogen ratio (S2 - / NO3-), can achieve the sulphide oxidation process step by step (S2- →S0) and nitrate reduction process of electron transfer balance, so as to realize simultaneous desulfurization and denitrification can be recycled to the elemental sulfur.

Under the condition of mixed culture, nitrite denitrification process can be either completely autotrophic or completely heterotrophic. It could also be a mixture of autotrophic and heterotrophic. At the same time, the excessive oxidation of sulfur is the main metabolic pathway. The accumulation of elemental sulfur depends on the proportion of water intake, nitrogen and sulfur, and the acidity and alkalinity.

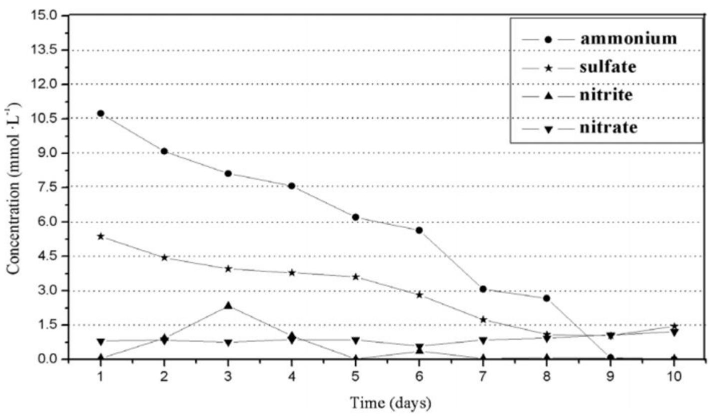

Figure 4: Batch test result for the measurement of ammonium, sulfate, nitrite and nitrate concentrations in anaerobic serum bottles with $(NH_4)_2SO_4$ as the sole substrate

Adopts full hybrid single reactor dealing with organic wastewater that are rich in sulfates and nitrates, due to produce acid bacteria, methane-producing bacteria, SRB, sulfur autotrophic denitrification bacteria and heterotrophic denitrifying bacteria complex competitive relationship between the function such as flora, it is difficult to obtain ideal elemental sulfur conversion rate. Therefore, a three-stage process is used for organic wastewater containing sulphate and ammonia nitrogen. The disadvantages of this method are obvious: the process is long and the operating conditions of the reaction are difficult to control. Additional carbon sources and oxygen are needed to increase energy consumption and processing costs; High concentration of HS- inhibits microbial activity.

$$SO_4^{2-} + COD \rightarrow HS^- + CO_2 \quad (10)$$

4. Conclusion

The pH value has obvious influence on anaerobic ammonia oxidation process. When the pH is >, 8. At 5, the activity of anaerobic ammonia oxidized sludge decreased, and began to lose the characteristics of anaerobic ammonia oxidation. The removal of NH+ 4-n decreases, while the removal of NO2- N is negative. Adjust reaction pH, change the reactor anaerobic ammonia oxidation bacteria dominant position and make the sulfate type anaerobic ammonia oxidation in a dominant position, can realize sulfate type anaerobic ammonia oxidation fast start.

Sulfate type anaerobic ammonia oxidation of nitrogen in the wastewater can be sulfur removal at the same time, avoid the ammonia nitrogen, sulfate respectively when handling process is not stable, low removal efficiency, and at the same time in the desulfurization of recovery of elemental sulfur, realize resource recycling, at the same time does not produce secondary pollution. The reaction process of sulphate anaerobic ammonia oxidation as an integrated desulfurization and desulfurization process, it has a very wide application prospect, but its application is affected by the long time and mechanism of the reaction. Therefore, the following aspects should be strengthened in the future. On the basis of the quantized reaction product, the research on the reaction mechanism and the physiological and biochemical characteristics of the functional microorganism is studied, and a highly effective and controllable reaction system is constructed. Analyze the difference of starting factors such as reactor and sludge source, shorten start-up time and optimize reaction process.

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