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Original scientific paper

Deep Denitrification of Domestic Sewage by Sulfur-based Mixotrophic Denitrification Filter

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Abstract: As a result of relevant policies and regulations, most wastewater treatment plants are faced with upgrading to further improve the level of effluent targets. To this end, this paper conducts an experimental study on deep denitrification in the sulfur Oyster shells mixotrophic nitrification filter process using sulfur as filler. During the experiments, when the water temperature in the mixotrophic pool was 15 °C, the nitrogen load of the inflow was 7.3×10^{-3}kg/m$^3 \cdot d$ and HRT equaled to 3.5 h, the average *TN* concentration in the effluent is 3.42 mg/L, and the *TN* removal rate reaches 54.49%, which can stably meet the core control area standard in the "Discharge Standard of Water Pollutants in Daqing River Basin" (DB13/2795-2018) and are the best operating parameters during the experimental period. The test results show that oyster shells can provide a large amount of alkalinity, alleviating the pH drop in the water column and effectively mitigating the acidification of the water column. Based on experimental calculations, without considering the loss of packing material, the operating cost of the sulphur-mixed denitrification filter process is reduced by $ 0.191 per tonne of water compared with the existing deep treatment unit in the WWTP. The above results show that the sulphur mixer denitrification filter has the ability to degrade the secondary effluent *TN* in depth, which provides some experimental basis for the sulphur mixer denitrification filter to be used as a deep treatment unit.

Keywords: advanced treatment; operation cost; oyster shell; sulfur-based mixotrophic denitrification

1 INTRODUCTION

In recent years, the discharge standards for sewage treatment plants have become stricter, resulting in high or unstable total nitrogen index values in the effluent of existing sewage treatment plants. How to further improve the denitrification capacity has become the primary consideration of sewage treatment plants during their upgrading and renovation [1-3]. At present, sewage treatment plants often have magnetic coagulation filters, aerated biological filters, activated sand filters, high-efficiency fiber filters, fiber rotary filters, high-density sedimentation tanks, etc. as enhanced deep denitrification unit [4]. The above-mentioned advanced treatment unit has been widely used in sewage treatment plants, but a series of problems have emerged, such as high power consumption, high head loss, high equipment costs, high maintenance costs, and complex equipment management processes. Traditional heterotrophic denitrification deep denitrification process microorganisms will reproduce in large quantities in a suitable environment, which can quickly achieve good nitrogen removal, and its start-up cycle is shorter, and it can be well adapted to different types of wastewater; although it has a long history of development, and the application of the technology is mature and extensive, heterotrophic denitrification technology also has shortcomings at the same time. For example, heterotrophic denitrifying bacteria grow and multiply quickly, and sludge production is high, which easily produces a large amount of residual sludge in the activated sludge system and increases its subsequent treatment and disposal costs. Compared with the traditional advanced treatment unit, the use of lower-cost sulfur-based mixotrophic denitrification filter for deep purification of sewage needs neither the addition of a large amount of carbon sources and nitrogen and phosphorus removal agents, nor the installation of complex power consumption equipment, becoming a new direction of current research. The sulfur-based mixotrophic denitrification is a reaction system combining the autotrophic system and heterotrophic system. Autotrophic denitrification uses autotrophic microorganism to convert nitrate nitrogen in sewage into nitrogen with elemental sulfur or its compounds as reaction electron donor, which are converted into sulfate radical [5]. This technology features low cost of elemental sulfur, less sludge production, and fast denitrification [6]. Denitrification is more stable and effective than heterotrophic and autotrophic denitrification. Mixotrophic is autotrophic and heterotrophic denitrification. Microorganisms share the nitrogen load in the water body, compared with pure heterotrophic denitrification, the carbon source supply is insufficient to meet only part of the growth of heterotrophic bacteria, so there is no risk of adding too much carbon source to ensure the quality of the effluent. At present, autotrophic and heterotrophic denitrification has more research results, but the process application of mixed nutrient denitrification is still immature, there is no optimal filler combination that can be referred to, the factors that may affect the mixotrophic denitrification and their degree of influence are still unclear, and the proportion of autotrophic, heterotrophic and parthenotrophic denitrifying bacteria in the activated sludge is also more variable, so there is still a lot of room for research on the mixotrophic denitrification. Therefore, there is still much room for research on denitrification. Current experimental studies using mixotrophic denitrification processes for nitrogen removal are numerous; for example, Peng's coupled ecological floating bed constructed using an iron base found that the presence of plant organisms improved iron-mediated denitrification and heterotrophic denitrification, and that mixed nutrient denitrification played an important role in nitrogen removal [7]. Pang et al. [8] studied the denitrification performance of a new mixotrophic system with pyrite (FeS_2) and biodegradable polymer complex (PLA/PHBV/rice husk, PPRH) as electron donor. After 12 days of operation, the average nitrate removal rate of the mixotrophic system (16.3 - 40.6 mg-N/L/d) was 37% higher than the combined removal rate of heterotrophic system and autotrophic system. It was found that denitrification performance and microbial communities were explored by varying the molar ratio of influent C/N/S. The mixotrophic system did enhance denitrification performance and provided a theoretical basis for the establishment of an efficient biological denitrification system [9]. It has been found that oyster shell is a kind of biological resource with strong adsorption and exists in large quantities in nature, so the resource utilization of oyster shell resources in wastewater treatment has become a research object for many scholars. Some studies show that the addition of rough and porous oyster shells with large surface area, has certain adsorption properties, which can not only provide alkalinity for autotrophic denitrification process, but also provide a growth environment for bacteria [10]. The author conducted field trials in a city wastewater treatment plant, with domestic wastewater as the treatment object, the front-end process for AAO biochemical treatment, designed with sulphur oyster shells, organic carbon sources as electron donor mixotrophic denitrification filter, research paper depth treatment secondary effluent process of pollutant degradation change law, analysis of the role of the depth treatment secondary effluent trend. It provides a realistic reference value for the application of the mixed culture denitrification filter technology with sulphur and oyster shells as mixed packing material in the existing deep nitrogen removal. The article includes the materials and methods required for the experiment, analysis of the results and conclusions.

2 MATERIALS AND METHODS

2.1 Test Device

The sulfur mixotrophic denitrification test system is constructed for the experiment. The water is supplied from the bottom to the top. The reaction tanks are all made of organic glass, with the size of $\Pi \times r^2 \times H = \Pi \times \left(0.17\,\mathrm{m}\right)^2 \times 1.7\,\mathrm{m}$. The schematic diagram of the device is shown in Fig. 1. The bottom is equipped with an inlet and a backwash water pipe. The secondary effluent enters the water tank through a peristaltic pump from the inlet pipe, passes through the packing layer, and is discharged from the upper outlet of the filter. The backwash water is pumped into the backwash water pipe at the top of the filter and enters the filter.

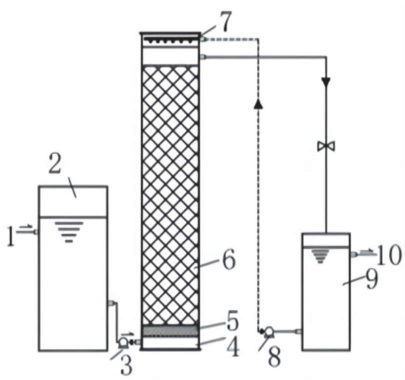

Figure 1 Diagram of the installation

Note: 1. Water inlet; 2. Water tank; 3. Inlet peristaltic pump; 4. Distribution reservoir; 5. Filter supporting bed; 6. Packing layer; 7. Backwash pipe; 8. Backwash peristaltic pump; 9. Outlet sump; 10. Water outlet

2.2 Test Packing

The height of the filter supporting bed is 0.1 m, the packing layer, 1.3 m, and the occupied volume of the packing layer is 0.12 m^3. The actual filling rate of the denitrification filter with sulfur and oyster shell as filler is 85%. The packing layer is packed according to the volume ratio of sulfur particles to oyster shell 1:1, and each volume of the two is 0.5 m^3. The main performance parameters are as follows: the sulfur particles were spherical or ellipsoid with a diameter of 3.0 - 5.0 mm; the diameter of oyster shell ranges from 1.5 to 4.0 cm; the pebbles of the supporting bed are spheres with a diameter within the range of 0.5 -1.0 cm. The packing is shown in Fig. 2 and Fig. 3.

Figure 2 Elemental sulfur

Figure 3 Oyster shell

2.3 Seeding Sludge

In this experiment, the sludge from the sludge enrichment tank of a sewage treatment plant was treated and used to start the reactor.

2.4 Sewage Sources

The test water source was the secondary effluent from the biochemical reaction tank of a municipal wastewater treatment plant.

2.5 Experimental Method

NH_4^+−N: Nessler's reagent spectrophotometry; NO_3^-−N: UV spectrophotometry; *TN*: Alkaline potassium persulfate ultraviolet spectrophotometry; pH: portable analyzer; Water temperature: Probe-type thermometer.

2.6 Reactor Operating Condition

According to different operating conditions of the reactor, the specific operating conditions of each stage of the test are shown in Tab. 1.

Table 1 Statistics of spring operation parameters of filter tank

Stage	AAO Reactor HRT/h	Inflow of the Mixotrophic Pool, *L/h*	Water body temperature / °C	Mixotrophic pool HRT/h
I	10	77.15	6 - 8	2.0
II	10	154.30	6 - 10	1.0
III	10	77.15	10 - 15	2.0
IV	10	51.43	12 - 16	3.0
V	10	44.09	15 - 18	3.5

The first stage is the start-up phase of the filter with a controlled HRT of 2 h. The stable operation starts from stage II and a different HRT is controlled at each stage.

2.7 Startup of the Reactor

The AAO reactor is separately cultured after sludge inoculation, and the mixotrophic pool is started at the same time. The method adopted is to simultaneously and continuously add organic carbon sources and sulfur sources during the start-up stage of the reactor, and after the preliminary acclimation and culture of activated sludge is completed, it was inoculated into the reactor [11]. Firstly, the sludge required for start-up is loaded into a sealed bucket, and it was kept stand for a while to restore to anoxic environment, then 5 L of pre-configured 100 mg/L potassium nitrate solution was injected, being stirred well. The sodium thiosulfate is added every day for 5 consecutive days, and sodium acetate is added for acclimation for the last 5 days. 30 L of the above-mentioned acclimated sludge was inoculated to the filter, and a small amount of organic carbon sources was added several times to promote the acclimation and culture of activated sludge. The packing layer of the filter is composed of sulfur and oyster shells, and the size and shape of oyster shells are different. In order to ensure that the volume ratio of sulfur particles in the filling layer and oyster shells is 1:1, and that the water flow rate at the bottom of the reactor is faster, a certain number of large oyster shells should be placed at the bottom first when adding, which can play a certain role in supporting and buffering. Each time when a certain amount of oyster shells is added, a certain amount of sulfur particles are put into the filter at the same time. Such alternant addition can not only ensure the overall stability of the filter, but also increase the porosity of the packing layer, providing more living space for microorganisms.

2.8 Reactor Water Supply

After the reactor is filled with the corresponding packing, the acclimated activated sludge is inoculated into the reactor, connecting the AAO reactor and the mixotrophic tank. The secondary effluent after the AAO treatment is eventually stored in the tank and injected into the mixotrophic tank through a peristaltic pump. After the completion of the water supply test, bubbles with a small amount of sludge float up among the pores of the packing layer. This is because N_2 generated by the reaction makes the flocculent sludge rise. In order to maintain the stability of the effluent, the work of cleaning impurities on the water surface is timely taken.

3 RESULTS AND ANALYSIS

3.1 Deep Nitrogen Removal Effect Under Different Hydraulic Loads

Stage I is the start-up stage. According to Fig. 4 it can be seen that the nitrogen removal capacity of AAO rapidly increased and remained stable in the start-up stage, but the effluent *TN* concentration is over 7 mg/L for a long time, and deep nitrogen removal is hindered. Therefore, the sulfur-based mixotrophic denitrification process shows the nitrogen removal capacity of the back-end deep nitrogen removal process strengthening system in the experiment.

Stage I was the start-up stage of the experiment. At this stage, a small amount of sodium acetate was added to the mixotrophic denitrification filter, and the nitrogen removal capacity of the system was improved significantly. The *TN* removal rate reached more than 40% on the 7th day, and the *TN* removal rate continued to rise with the experiment. The nitrogen removal load in the mixotrophic pool changed gradually with the acclimation process, and the removal load increased gradually. The following exposition is obtained according to Fig. 5. In stage I (Day 1 to Day10), the hydraulic load and influent nitrogen load were at the higher levels of 1.71 $m^3/m^2 \cdot h$ and 0.026 $kg/m^3 \cdot d$, respectively, and the HRT of the mixotrophic denitrification filter was 2 h. When the average influent *TN* concentration is 13.78 mg/L, the average effluent *TN* concentration is 9.76 mg/L, and the *TN* removal rate reaches 33.15%. At this stage, the average *TN* removal load is $7.5 \times 10^{-3} kg/m^3 \cdot d$. For the initial start-up of the sulfur mixotrophic denitrification filter, the heterotrophic reaction in the system was maintained by adding carbon sources. The operation effect also showed that in the process of systematic inoculation and culture of bacteria, a large amount of nitrate was degraded and transformed, and the proportion of autotrophic denitrification gradually increased, showing certain nitrogen removal ability in a relatively short time. In stage II (Day 11 to Day 15), the HRT of the mixotrophic denitrification filter was adjusted to 1 h, and the hydraulic load and influent nitrogen load were reduced to 1.71 $m^3/m^2 \cdot h$ and 0.019 $kg/m^3 \cdot d$, respectively. When the average influent *TN* concentration is 6.87 mg/L, the average effluent *TN* concentration is 5.25 mg/L, and the *TN* removal rate reaches 23.69%. At this stage, the average *TN* removal load is 6.0×10^{-3} $kg/m^3 \cdot d$. In stage III (Day 16 to 25), the HRT of the mixotrophic denitrification filter was further extended to 2 h, and the hydraulic load and influent nitrogen load were reduced to 0.86 $m^3/m^2 \cdot h$ and 1.29×10^{-2} $kg/m^3 \cdot d$, respectively. When the average influent *TN* concentration is 7.01 mg/L, the average effluent *TN* concentration is 4.29 mg/L, and the *TN* removal rate reaches 38.82%. In this stage, the average *TN* removal load is 5.0×10^{-3} $kg/m^3 \cdot d$, and the *TN* removal rate is 1.64 times larger than that of stage II. In stage IV (Day 26 to Day 40), the HRT of the mixotrophic denitrification filter was further extended to 3 h, and the hydraulic load and influent nitrogen load were reduced to 0.57 $m^3/m^2 \cdot h$ and 8.96×10^{-3} $kg/m^3 \cdot d$, respectively. When the average influent *TN* concentration is 7.19 mg/L, the average effluent *TN* concentration is 3.49 mg/L, and the *TN* removal rate reaches 51.77%. In this stage, the average *TN* removal load is 4.6×10^{-3} $kg/m^3 \cdot d$, and the *TN* removal rate is 1.33 times that of stage II.

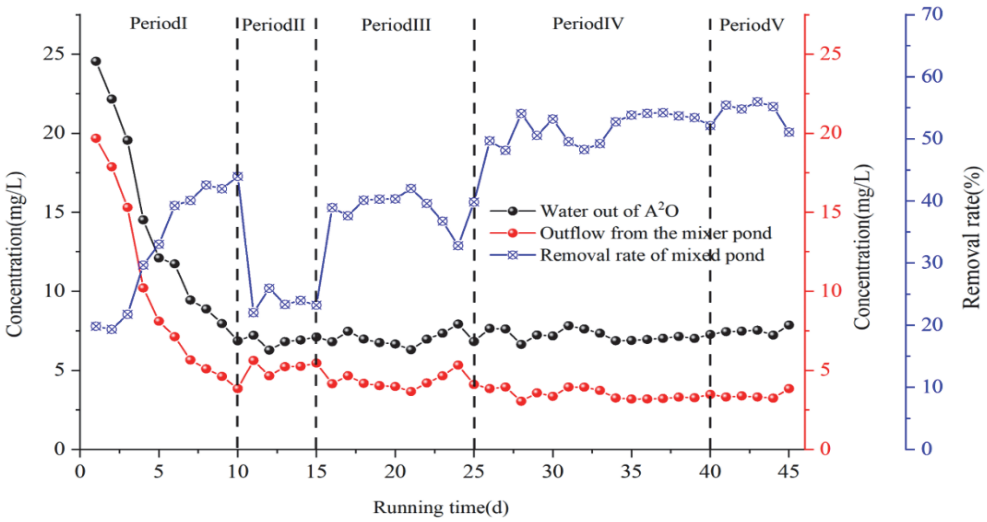

Figure 4 *TN* removal effect in mixotrophic ponds

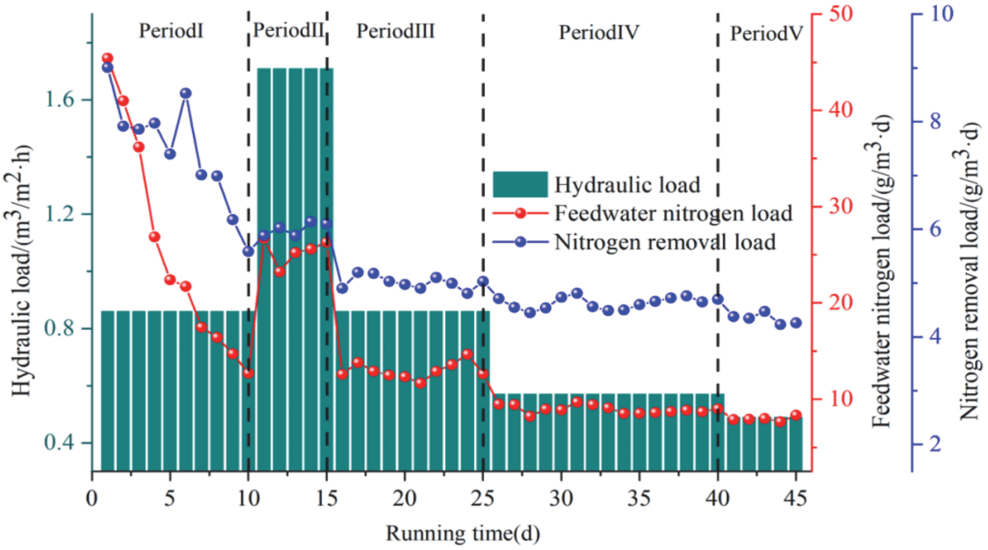

Figure 5 Hydraulic load and nitrogen load relationship

In the test phase V (Day 41 to Day 45), the HRT was extended to 3.5 h, and the hydraulic load and influent nitrogen load in this process were 0.49 $m^3/m^2 \cdot h$ and 7.9×10^{-3} $kg/m^3 \cdot d$. When the average influent *TN* concentration was 7.47 mg/L, the average effluent *TN* concentration was 3.42 mg/L. The *TN* removal rate reached 54.49%, and the *TN* removal rate increased by 2.7 percentage points compared with stage III. *TN* removal was increased by extending the HRT, a large amount of nitrate nitrogen in the water was degraded, and inverse nitrate bacteria were maintained in high numbers in the system [12]. In comparison, it was found that as the hydraulic load of the filter tank and the influent nitrogen load were increased, the *TN* removal rate decreased, indicating that nitrogen could not be effectively removed in the filter under the condition of high hydraulic load. Under the premise of maintaining stable and deep nitrogen removal capacity of the system, increasing hydraulic load and influent nitrogen load to a higher level can reduce the reactor volume, which saves space and use cost. In the course of the second stage of the test, it was found that a large number of yellow striped and irregular aerobic bacterial colonies were attached to the upper wall of the mixotrophic denitrification filter and near the outlet, and in the late stage of the test, the bacterial colonies had already covered the smooth wall near the outlet, and it was assumed that they were also in the process of long-term bottom-up operation of the water body, and a large number of different kinds of bacteria suitable for this environment were growing in large quantities and attaching themselves to the wall of rough filters, and the formation of bacterial colonies might have a positive effect on the degradation of part of the nitrogen. In addition, the gradual rise of water temperature from stage I to stage V is also an influence factor on the deep nitrogen removal in the filter, in an experiment using autotrophic denitrification to treat actual nitrate contaminated groundwater, Demir et al. [13] found a significant decrease in denitrification efficiency when the temperature was reduced from 30 °C to 20 °C, suggesting that higher water temperatures are more suitable for microbial growth and that microbial metabolism is accelerated.

3.2 Nitrogen Transformation in Mixotrophic Pond

Fig. 6 further illustrates the conversion process of nitrogen elements in the mixotrophic tank. The nitrogen in the secondary effluent is still mainly NO_3^-–N and contains a small amount of NH_4^+–N. In the experimental stage V, when the average NO_3^--N concentration of influent water was 4.11 mg/L, the average NO_3^-−N concentration of effluent water was 0.58 mg/L and the average removal rate was 85.89%, indicating that NO_3^-−N could be removed through the mixotrophic denitrification. Under the condition that the average influent NH_4^+−N concentration is 0.59 mg/L, the average effluent NH_4^+−N concentration is 0.29 mg/L, and the average removal rate is 50.85%. The mixotrophic pool has a better degradation effect on NH_4^+−N in the water body. Meanwhile, the total content of NH_4^+−N and NO_3^-−N in the water body in each stage of the experiment is lower than the *TN* concentration, showing that there was dissolved organic nitrogen (DON) in the effluent of the mixotrophic ponds, and some studies showed that the secondary biochemical effluent treated with heterotrophic denitrification filter still contained 31.2% - 39.8% dissolved organic nitrogen (DON) [14]. The proportion of dissolved organic nitrogen (DON) in effluent *TN* is increasing, up to more than 50% [15, 16]. The mixotrophic denitrification filter itself does not have the environmental and technological conditions to degrade organic nitrogen in secondary effluent.

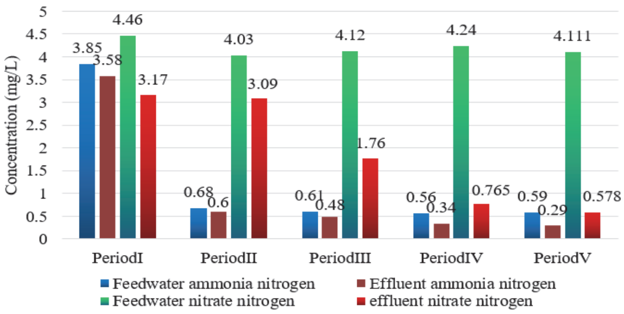

Figure 6 Nitrogen conversion in mixotrophic pond

3.3 Changes of pH before and after Denitrification in a Mixotrophic Denitrification Filter

BATCHELOR put forward the equation of sulfur autotrophic denitrification process:

$$1.1S^0 + NO_3^- + 0.76H_2O + 0.4CO_2 + 0.08NH_4^+ - N \rightarrow$$
$$0.08\ C_5H_7O_2N + 1.1SO_4^{2-} + 0.5N_2 + 1.28H^+$$

The above reaction equation shows that H^+ produced in sulfur autotrophic denitrification process is the main cause of acidification of water body, which consumes certain alkalinity under normal reaction conditions. According to relevant studies, the growth of D. desulfuricans itself is pH-dependent, and too high or how low the temperature is will inhibit the growth of D. desulfuricans [17]. The optimal denitrification pH value of thiobacillus denitrificans is 6.8, and the pH change in the mixotrophic tank is shown in Fig. 7. The floating pH range of the effluent from secondary sedimentation tank at each stage is within the range of 7.2 - 7.9, and the average pH value is 7.76. The effluent pH at the end of the mixotrophic denitrification filter mainly fluctuates between 6.8 and 7.8, and the average effluent pH is 7.36. The HRT of the mixotrophic denitrification filter was gradually extended from 1 h and the pH of the effluent at each stage decreased, but the decrease was small, indicating that autotrophic denitrification had become the main reaction process in the mixotrophic denitrification filter at this time [18]. Liu and Koenig [19] found that the autotrophic denitrification process using sulphur as an electron donor consumed approximately 4 g of alkalinity (in terms of $CaCO_3$) per g of nitrate nitrogen reduction, demonstrating that the rate of autotrophic denitrification during the mixotrophic process can be safeguarded by providing alkalinity in the water column to maintain a stable system pH, relying only on heterotrophic denitrification in this experiment. The alkalinity generated by heterotrophic denitrification alone was not sufficient to ensure stable denitrification performance, so the subsequent establishment of an operational strategy with an additional partial alkalinity source was necessary to reduce the dissolved solids increment in the effluent [20].

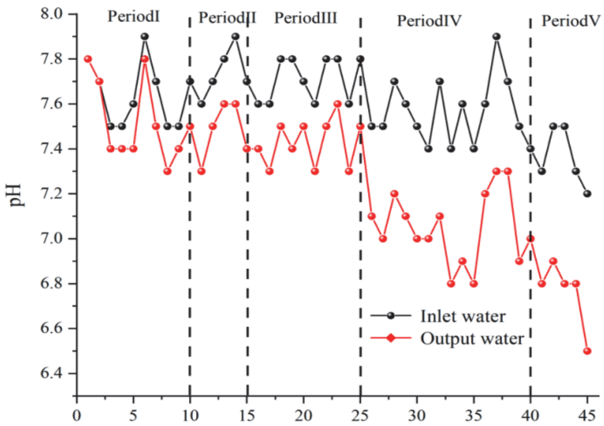

Figure 7 pH change of effluent water in each stage

4 OPERATIONAL PERFORMANCE COMPARISON
4.1 Effluent Quality Comparison

The average NH_4^+−N and average *TN* of effluent running in different stages during the effluent test of the sewage treatment plant were compared. As can be seen from Tab. 2, the effluent quality of the test system was slightly worse than that of the sewage treatment plant at the initial start-up stage, and in the stable operation stage of the test system, the average concentrations of NH_4^+−N and *TN* in the effluent from the mixotrophic denitrification filter are lower than the effluent level of the sewage treatment plant, indicating that when HRT of the mixotrophic tank is longer than 2 h, the deep nitrogen removal effect is obvious, and the effluent can maintain a stable state. However, compared with the NH_4^+−N data, there is no significant difference in the effluent concentration, while the *TN* concentration of the effluent from the test is lower than that of the effluent from the sewage plant, which is due to the continuous progress of autotrophy-heterotroph in the mixed denitrification filter, consuming a large amount of NO_3^-−N in the water.

Table 2 Comparison of wastewater treatment plant effluent and average effluent concentrations at each stage of the test

Time / d	NH_4^+−N / mg/L		*TN* / mg/L	
	Water plant effluent	Test effluent	Water plant effluent	Test effluent
I	0.35	3.58	5.52	7.45
II	0.32	0.60	5.68	5.25
III	0.37	0.48	5.86	4.29
IV	0.36	0.34	5.24	3.49
V	0.36	0.29	4.96	3.42

4.2 Comparison of Operation Cost

Cost reduction and efficiency enhancement is a major focus of current research. The sulfur mixotrophic denitrification process features high efficiency and low energy consumption [21]. Therefore, the operation cost of treatment of per ton of water in the advanced treatment unit after secondary effluent of the actual sewage treatment plant was calculated and compared with the operation cost of treating per ton of water in the mixotrophic denitrification filter, and the analysis is as follows. According to the calculation in Tab. 3, PAC and PAM are required to be added in the high-density sedimentation tank in the actual process, and the dosage is 40 and 1 mg/L respectively. 10% PAC is calculated at the unit price of 1000 yuan/ton, and PAM is calculated at the unit price of 30000 yuan/ton. The cost of drug adding is about 0.07 yuan /m^3, and its power consumption equipment N equals to 51.75 kW. The comprehensive electricity price is 0.6 yuan /m^3, the converted electricity fee is 0.25 yuan /m^3, and the single operation cost is 0.32 yuan /m^3. The main operating cost of active sand filter is electricity loss, and the operating cost per unit is 0.17 yuan/m^3. Ultrafiltration membrane water purification technology is widely used [22], and the daily operating costs of its technical workshops include the cost of electricity for the equipment, the chemical cleaning fee, backwashing cost, power consumption equipment including water pump, dosing pump, multi-group automatic control box, indoor lighting facilities, etc. The electricity fee is calculated by 0.78 yuan/(kw·h), and the reagents used mainly include NaClO, NaOH, etc. Among them, the power consumption cost of per ton of water running at 10 L/(m^2·h) flux is 0.04 yuan/m^3, the backwashing agent cost of 10% NaClO is 0.016 yuan/m^3, the chemical cleaning cost of HCl, NaOH and citric acid is 0.06 yuan/m^3, and the single operation cost is 0.116 yuan/m^3. The total treatment cost of the advanced treatment unit of the sewage treatment plant is 0.606 yuan/m^3, among which the main cost source is the electricity cost loss of various single supporting equipment.

Table 3 Operating costs for tons of water deep treatment unit of wastewater treatment plant

Cost loss unit	High-density sedimentation tanks	Active sand tank	Ultrafiltration membrane water purification workshop
Energy charge	Power consumption equipment N = 51.75 kW; the comprehensive price of electricity is 0.6 yuan/m^3, converted to 0.25 yuan/m^3	2 air compressors, single machine N = 22 kW; 1 cold drying machine, N = 1.5 kW, comprehensive operation electricity charge 0.17 yuan/m^3	Running at 10 L/(m^2·h) flux; the electricity consumption of a ton of water is 0.04 yuan/m^3
Pharmaceutical cost	The dosage of PAC is 40 mg/L, 10% PAC is calculated at the unit price of 1000 yuan/ton, and the cost of PAC is 0.04 yuan/m^3	No	10% NaClO backwashing reagent cost 0.016 yuan/m^3
	The dosage of PAM is 1 mg/L. If the unit price of PAM is 30000 yuan/ton, the cost of PAM is 0.03 yuan/m^3	No	Chemical cleaning fee of HCl, NaOH and citric acid is 0.06 yuan/m^3
Unit operating cost / yuan/m^3	0.32	0.17	0.116
Total operating cost / yuan/m^3	0.606		

Table 4 Operation cost of treatment of per ton of water in mixotrophic denitrification filter

Operating cost of mixotrophic denitrification filter	
Energy charge	Inlet water pump N=0.03kW; the comprehensive electricity price is 0.6 yuan /m^3, converted to 0.41 yuan /m^3
Padding loss cost / yuan/m^3	Cost of elemental sulfur loss 0.0027 yuan/m^3 and the loss cost of oyster shell is 0.0021yuan/m^3
Total operation cost / yuan/m^3	0.415 yuan/m^3

According to the analysis in Tab. 4, the thickness of the filter material in the sulfur mixotrophic denitrification filter showed no obvious signs of loss during the test, and the loss of sulfur elemental substance and oyster shell was calculated according to the reaction equation. The market unit price of sulfur elemental substance was calculated as 1,500 yuan/ton, the $CaCO_3$ content of oyster shell was calculated as 90%, and the market unit price was calculated as 680 yuan/ton. The packing cost is calculated as 0.0048 yuan /m^3. The running electricity cost mainly comes from the water pump. The inlet water pump needs continuous operation, and the backwash running times are few and each running time is short. Its power consumption is not taken into consideration. The total treatment cost of mixed denitrification filter is 0.415 yuan/m^3. The power consumption of the inlet water pump is mainly calculated, which is mainly the 0.03 kW small water pump, the electricity price is calculated as 0.6 yuan/kW·h, the direct operation electricity cost is 0.41 yuan/m^3, and the total treatment cost of the mixotrophic denitrification filter is 0.415 yuan/m^3. Based on the cost analysis of actual operation, it can be found that the deep treatment with sulfur mixotrophic denitrification filter avoids the cost loss caused by a large number of added drugs, and the cost of a ton of water treatment is reduced by 0.191 yuan. This test is only for the small pilot stage of the operating cost analysis, if the pilot or large-scale industrial applications need to focus on the loss of sulfur and oyster shells to analyse and summarize the continuous use of the filler life cycle of the filter pond. In general, the filter form is simple, the process is simple and effective, has the ability of deep nitrogen removal, and the operating cost is not high, but from the practical application of the promotion of long-term experimental verification is needed.

5 CONCLUSIONS

(1) When the water temperature of the mixotrophic pool is 15 - 18 °C, the influent nitrogen load is 7.3×10^{-3} kg/m^3·d, and when the HRT is 3.5h, the average effluent TN concentration is 3.42 mg/L, and the TN removal rate reaches 54.49%. It can stably reach the standard for the core control area regulated in 'Discharge Standard of Water Pollutants in Daqing River Basin" (DB13/2795-2018), which is the best operating parameter during the test.

(2) After the treatment in the mixotrophic tank, the pH of the secondary biochemical effluent decreased, indicating that the reducing S^0 participated in the reduction process of NO_3^-−N under the action of autotrophic denitrifying bacteria. However, due to the existence of oyster shells, a large amount of alkalinity is provided, making the pH reduction effect not obvious.

(3) According to the cost analysis, comparing the sulfur mixotrophic denitrification filter with the advanced treatment unit of the sewage treatment plant, the per ton of water treatment cost of the former is 0.191 yuan less than that of the latter. If cost losses are to be projected more scientifically and rationally, the level of experimental scale needs to be increased and validated over time.

The experiment did not further explore and validate the process share of heterotrophic denitrification and autotrophic denitrification in the mixotrophic denitrification process, and the experimental period was relatively short, so there are some limitations, and the long-term operational effectiveness should be considered.

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6 REFERENCES

[1] Xiao, J. & Chu, S. (2015). A novel bamboo fiber biofilm carrier and its utilization in the upgrade of wastewater treatment plant. *Desalination and Water Treatment*, *56*(3), 574-582. https://doi.org/10.1080/19443994.2014.940397

[2] Dong, B., Li, Y. R., Li, X. Y., Chen, Z. T., Ge, Y., & Zhang, R. (2022). Construction of an MFC anaerobic-aerobic coupled denitrification system and its performance enhancement method. *Journal of New Materials for Electrochemical Systems*, *25*(4),301-307. https://doi.org/10.14447/jnmes.v25i4.a11

[3] Zhang, X., Liu, J. L., & Ma, L. (2023). Experiments on mixotrophic denitrification under different hydraulic loads and water temperatures. *International Journal of Heat and Technology*, *41*(1), 117-124. https://doi.org/10.18280/ijht.410112

[4] Li, Y. F., Wang, X., & Liu, S. (2012). Engineering example of A2O-high density sedimentation tank-filter tank process in the treatment of municipal sewage. *Applied Mechanics and Materials*, *178*, 671-675. https://doi.org/10.4028/www.scientific.net/AMM.178-181.671

[5] Woo, Y. C., Lee, J. J., & Kim, H. S. (2022). Removal of nitrogen from municipal wastewater by denitrification using a sulfur-based carrier: A pilot-scale study. *Chemosphere*, *296*, 133969. https://doi.org/10.1016/j.chemosphere.2022.133969

[6] Ren, X., Wang, Y., Wan, J., Yan, Z., Ma, Y., Zhang, G., & Zhu, B. (2022). The nitrogen removal performance and functional bacteria in heterotrophic denitrification and mixotrophic denitrification process. *Water*, *14*(22), 3603. https://doi.org/10.3390/w14223603

[7] Peng, Y., Gu, X., Yan, P., Sun, S., Zhang, M., Tang, L., & He, S. (2023). Mixotrophic denitrification improvement in ecological floating bed: Interaction between iron scraps and plant biomass. *Science of The Total Environment*, 861, 160718. https://doi.org/10.1016/j.scitotenv.2022.160718

[8] Pang, Y., Hu, L., & Wang, J. (2022). Mixotrophic denitrification using pyrite and biodegradable polymer composite as electron donors. *Bioresource Technology*, *351*, 127011. https://doi.org/10.1016/j.biortech.2022.127011

[9] Zheng, S., Liu, X., Yang, X., Zhou, H., Fang, J., Gong, S., Yang, J., Chen, J., Lu, T., Zeng, M., & Qin, Y. (2022). The nitrogen removal performance and microbial community on mixotrophic denitrification process. *Bioresource Technology*, *363*, 127901-127901. https://doi.org/10.1016/j.biortech.2022.127901

[11] Wang, P. Q. (2018). *Denitrification performanceand bacterial communities in a mixotrophic denitrification system*. Shanghai Jiaotong University, Shanghai, China.

[12] Yuan, S., Zhu, W., Guo, W., Sang, W., & Zhang, S. (2022). Effect of hydraulic retention time on performance of autotrophic, heterotrophic, and split-mixotrophic denitrification systems supported by polycaprolactone/pyrite: Difference and potential explanation. *Water Environment Research*, *94*(12), e10820. https://doi.org/10.1002/wer.10820

[13] Demir, Ö., Atasoy, A. D., Çalış, B., Çakmak, Y., Di Capua, F., Sahinkaya, E., & Uçar, D. (2022). Impact of temperature and biomass augmentation on biosulfur-driven autotrophic denitrification in membrane bioreactors treating real nitrate-contaminated groundwater. *Science of The Total Environment*, *853*, 158470. https://doi.org/10.1016/j.scitotenv.2022.158470

[14] Goli, T., Jathan, Y., Yang, Y., Pagilla, K. R., & Marchand, E. A. (2023). Pilot-scale demonstration of dissolved organic nitrogen removal from an advanced water reclamation facility using enhanced coagulation. *Science of The Total Environment*, *877*, 162864. https://doi.org/10.1016/j.scitotenv.2023.162864

[15] Haidong, L., Kewei, G., & Jinju, K. (2018). Removal characteristics of dissolved organic nitrogen and its bioavailable portion in a postdenitrifying biofilter: effect of the C/N ratio. *Environmental Science & Technology: ES&T*, *52*(2), 757-764. https://doi.org/10.1021/acs.est.7b05115

[16] Liu, H., Jeong, J., Gray, H., Smith, S., & Sedlak, D. L. (2012). Algal uptake of hydrophobic and hydrophilic dissolved organic nitrogen in effluent from biological nutrient removal municipal wastewater treatment systems. *Environmental Science & Technology*, *46*(2), 713-721. https://doi.org/10.1021/es203085y

[17] Zou, G., Papirio, S., Lakaniemi, A. M., Ahoranta, S. H., & Puhakka, J. A. (2016). High rate autotrophic denitrification in fluidized-bed biofilm reactors. *Chemical Engineering Journal*, *284*, 1287-1294. https://doi.org/10.1016/j.cej.2015.09.074

[18] Lu, K. & Liu, Z. (2022). The formation of refractory dissolved organic nitrogen from free amino acids in the ocean. *Geophysical Research Letters*, *49*(18), e2022GL100041. https://doi.org/10.1029/2022GL100041

[19] Liu, L. H. & Koenig, A. (2002). Use of limestone for pH control in autotrophic denitrification: Batch experiments. *Process Biochemistry*, *37*(8), 885-893. https://doi.org/10.1016/S0032-9592(01)00302-8

[20] Pan, H., Cui, M. H., Zhang, C., Lan-Ying, L., Jing, L., Qian, J., Xue-Dong, Z., Zhi-Yong, Z., Yan, Z., He, L. (2022). Alkalinity regulation in a sulfur autotrophic denitrifying filter substantially reduced total dissolved solids and sulfate in effluent. *Bioresource Technology*, *348*, 126751. https://doi.org/10.1016/j.biortech.2022.126751

[21] Hong, X., Tang, L., Feng, H., Zhang, X., & Hu, X. (2022). Agriculture waste as slow carbon releasing source of mixotrophic denitrification process for treating low C/N wastewater. *Separations*, *9*(10), 323. https://doi.org/10.3390/separations9100323

[22] Li, M., Wen, L., & Chen, Y. (2018). Application of ultrafiltration membrane technology in environmental engineering water treatment. *Academic Journal of Environment & Earth Science*, *4*(8), 20-24. https://doi.org/10.25236/AJEE.2022.040804

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