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Sulfur-based autotrophic denitrification from the micro-polluted water

Weili Zhou*, Xu Liu, Xiaojing Dong, Zheng Wang, Ying Yuan, Hui Wang, Shengbing He

School of Environmental Science and Engineering, Shanghai Jiaotong University, Shanghai 200240, China

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ABSTRACT

Eutrophication caused by high concentrations of nutrients is a huge problem for many natural lakes and reservoirs. Removing the nitrogen contamination from the low C/N water body has become an urgent need. Autotrophic denitrification with the sulfur compound as electron donor was investigated in the biofilter reactors. Through the lab-scale experiment, it was found that different sulfur compounds and different carriers caused very different treatment performances. Thiosulfate was selected to be the best electron donor and ceramsite was chosen as the suitable carrier due to the good denitrification efficiency, low cost and the good resistibility against the high hydraulic loads. Later the optimum running parameters of the process were determined. Then the pilot-scale experiment was carried out with the real micro-polluted water from the West Lake, China. The results indicated that the autotrophic denitrification with thiosulfate as electron donor was feasible and applicable for the micro-polluted lake water.

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Introduction

Many important lakes in China, like the West Lake, Taihu Lake, and Chaohu Lake, lie in the thickly populated agricultural areas. As nitrogen fertilizers are widely used in farming and planting, the nitrogen compounds are flushed into the rain, enter the nearby lakes, and finally cause the eutrophication. Moreover, the large amount of nitrogen in the water bodies also threaten the fishery and human health greatly because ammonium is toxic to aquatic organisms, and nitrite is a dangerous cancer inducer which may cause the disease of methemoglobinemia in infants. Therefore, nitrogen removal becomes a very important work. On the other hand, under the natural conditions all forms of nitrogen tend to transform into nitrate and exist stably in the surface water as nitrate, for example, nitrate in West Lake water accounts for 60%–70% of the total nitrogen. Hence denitrification becomes an urgent

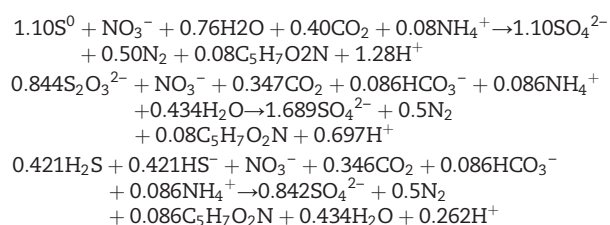
issue in preventing water eutrophication and controlling the nitrogen pollution.

As both nitrogen and carbon pollutants in the natural water bodies are of relatively low concentrations (that is why it is called micro-pollution), mostly no more than 10 mg/L, the treatment process has to be specially designed for this character. Nowadays the heterotrophic denitrification is the most commonly-used denitrification process. It needs the organic carbon to provide electrons for the reduction of nitrate, and at the same time, to provide carbon source for the metabolism of heterotrophic microorganisms. However, there are some problems in this process, including residual organic matters which may cause the secondary contamination, and the high amount of excess sludge which needs final disposal.

Autotrophic denitrification can be a useful alternative to the heterotrophic one. Autotrophic denitrification is accomplished by autotrophic denitrifying bacteria which utilize the inorganic

* Corresponding author. E-mails: weilizhou@sjtu.edu.cn, wei_lizhou@hotmail.com (Weili Zhou).

materials as electron donors and carbon source. Although the slow growth of autotrophic bacteria may cause lower treatment efficiency, it brings about two important advantages for the autotrophic process (Soares, 2002; Rocca et al., 2007; Sierra-Alvarez et al., 2007). First, it needs no external organic carbon source (methanol, ethanol or acetate) which lowers the risk of secondary contamination. Second, lower cell yield and sludge production minimize the disposal of sludge. Presently studies on autotrophic denitrification have been divided into two directions: one is hydrogen-based (Lee and Rittmann, 2003; Wang and Qu, 2003), in which hydrogen gas is used, and the other is sulfur-based, in which sulfur compounds, such as sulfide and elemental sulfur, are utilized (Moon et al., 2004, 2006) as electron donors. Due to the danger and difficulties of handling hydrogen gas, the sulfur-based process has gained more and more attention. The stoichiometric equations of sulfur-based autotrophic denitrification can be described as follows (Koenig and Liu, 2001).



So far the studies of sulfur-based autotrophic denitrification have been mostly on using elemental sulfur as electron donors. Park et al. (2002) proved the feasibility first. They investigated the impact of influent concentration and nitrogen loading rate (NLR), and verified that 95% of nitrate could be removed when the influent nitrate achieved 175 mg/L and the NLR reached 2.46 kg N/(m³·day). Nitrogen removal was closely related to the influent concentration and the NLR. Moon et al. (2006) found that the size of sulfur granules greatly affected the denitrification process. Smaller granules brought better efficiency, but if the granules were too small, they might be flushed out, together with bacteria on them. Due to the consumption of alkali in the process, lime is often used in the form of sulfur-limestone in order to provide the sufficient alkalinity. Later, Sierra-Alvarez et al. (2007) found that the 7.3 mmol/L nitrate was removed by 95.9%, and the nitrite in the effluent was very low. The production of nitrogen gas followed the stoichiometric equation that Koenig and Liu (2001) put forward. A few species of autotrophic denitrifiers have been found to utilize elemental sulfur meanwhile reducing nitrate to nitrogen gas, such as *Thiobacillus denitrificans* (Moon et al., 2008; Koenig et al., 2005) and *Thiomicrospira denitrificans* (Brettar et al., 2006).

Using sulfide as electron donor represents another experience for the simultaneous removal of nitrate and sulfide from wastewaters. For example, Vaiopoulou et al. (2005) found that almost all the 110 mg/L sulfide was removed while the denitrification efficiency achieved 100%, and S/N ratio and sulfide concentration were crucial impact factors in this process. Lu (2009) studied the mechanism of this process and revealed that at high NLR the sulfide was first partly oxidized into elemental sulfur, but at the low concentration and long hydraulic retention time (HRT), most sulfide was oxidized into sulfate directly. However, Fajardo et al. (2014)

studied the influence of some factors on the denitrification process and found that sulfide concentration of 200 mg/L could inhibit the process, and nitrite of 48 mg/L could inhibit it by 50%. Moraes et al. (2012) also have similar conclusion about the inhibition of sulfide.

Eutrophication is a chronic disease for many natural lakes and rivers. The characters of micro-pollution, that is, low concentrations of pollutants and low C/N ratio, make the biological treatment even more difficult. Sulfur-based autotrophic denitrification may provide a cure for this disease. However, its real application has never been reported. On the other hand, very few studies put attention on another possible electron donor, thiosulfate. In order to understand the applicability of sulfur-based autotrophic denitrification, this study focuses on the nitrate removal from micro-polluted water, aiming to find out the optimal type of sulfur-based electron donor, the suitable working conditions, and the feasibility of real application.

1. Materials and methods

1.1. Experimental set-up

Five lab-scale up-flow biofilters, as shown in Fig. 1, were used for the continuous denitrification from the nitrate-rich water. Four reactors (named as L1, L2, L3 and L4) were identical, consisting of a cylindrical glass tube with the inner diameter of 88 mm, effective height of 0.5 m and effective volume of about 3.0 L. The fifth (L5) reactor was of the same volume but with the inner diameter of 62 mm and height of 1.0 m. Two pilot-scale biofilters were used to verify the applicability. The first (named as P1) up-flow biofilter was made of PVC, with the inner diameter of 300 mm, height of 4.2 m, the effective volume of 300 L, and designed full treatment capacity of 12 m³/day. The second pilot-scale (P2) reactor was a down-flow biofilter, a used rectangle tank made of concrete. It was divided into two cells, each with length of 4 m, width of 3 m, effective depth of 3 m (2 m of filter carrier and 1 m of extra height), and designed full treatment capacity of 900 m³/day.

Tap water was used in the lab-scale reactors as its nitrogen content was very similar to the micro-polluted surface water. Soluble sulfur compound, Na₂S or Na₂S₂O₃, was added at the S/N (mol/mol) ratio of 1.0, according to the nitrate concentration. Tap water in this city was acidic (pH about 6.0–6.2) so alkali was added during the domestication period, to adjust pH to 6.5–7.0. The water temperature around the year was from 5 to 30°C. For the pilot-scale reactors, the source water comes from Qiantang River and is pretreated with coagulating sedimentation process in a water pretreatment plant located by West Lake, Hangzhou, China. The pretreated water was pumped from the sedimentation tank into the pilot-scale reactors.

The ceramsites (diameter 5–10 mm) were used as the carrier for both lab-scale and pilot-scale reactors, yet when using the elemental sulfur as electron donor, the sulfur-limestone (diameter 5–8 mm) was used as the carrier and alkali at the same time. The reactors were seeded with digested sludge from the municipal wastewater treatment plant. No temperature controller was installed in order to simulate the natural temperature

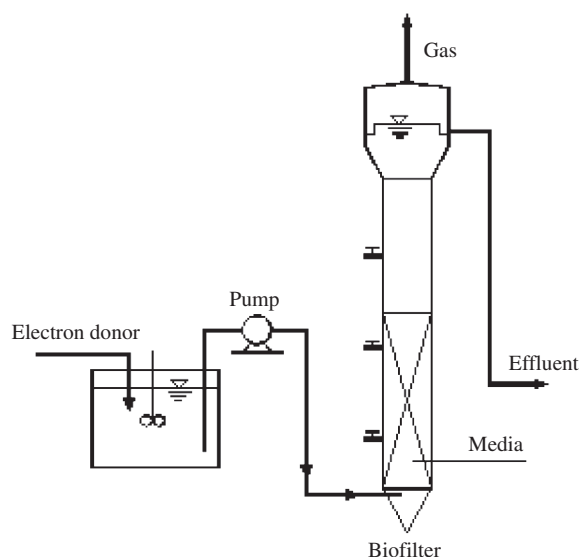


Fig. 1 – The schematic figure of the reactors.

variation. After contacting with the microorganisms, the effluent was sampled and measured for total nitrogen (TN), nitrate, nitrite, and sulfate.

1.2. Analytical method

Nitrate, nitrite and TN were determined according to the standard method (APHA, American Public Health Association et al., 1999). The ultraviolet spectrophotometric method was followed for TN and nitrate determination, while 1,2-Ethane diamine, N-1-naphthalenyl-, dihydrochloride spectrophotometric method was used for the nitrite measurement. Sulfate measurement was carried out using the ion chromatograph (MIC, Metrohm).

2. Results and discussion

2.1. Selection of reductive sulfur compound as electron donor

Selection of electron donors was carried out in three lab-scale reactors. Reactor L1 was packed with 2.0 L sulfur-limestone. The other two reactors, L2 and L3, were both packed with 2.0 L

ceramsites as carrier. The reactors were all fed with nitrate solution of 13 mg N/L, and L2 and L3 were added with Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$, respectively, at the S/N ratio (M/M) of 1.0.

All reactors have run for more than 150 days. Table 1 shows the denitrification performance of the reactors during the stable running period. All the three reactors were affected obviously by the HRT and the water temperature. Under 10°C, the denitrification efficiency was poor and unstable. Therefore, the comparison was made over two temperature zones: 10–20°C and above 20°C.

From Table 1, it was found that when the temperature varied between 10 and 20°C, 49.8% of the nitrate, and 40.0% of the TN could be removed in reactor L1, in which elemental sulfur was used as electron donor. For reactor L2, only 46.7% of nitrate and 36.7% of TN could be removed. Meanwhile, at the same HRT of 4 hr, nitrate and TN removal of reactor L3 could achieve 92.1% and 79.9% respectively. Moreover, the effluent nitrite differed with the electron donor, which revealed the different completion of the biological process. Due to the low solubility of elemental sulfur, the electron-providing ability was limited, causing the incomplete denitrification process. On the other hand, both Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$ are soluble, yet the denitrification performance with $\text{Na}_2\text{S}_2\text{O}_3$ turned out to be much more efficient.

When the temperature was above 20°C, the difference became even more obvious. L2 remained the most inefficient, and temperature increase did not improve the denitrification efficiency. However, both the sulfur and thiosulfate system were remarkably improved by higher temperature. More than 70% of the nitrate and TN were removed in L1, and L3 removed more than 90% of TN as well as almost all the nitrate. The effluent nitrite in all reactors remained low, especially in L3, even when the HRT was shortened to 30 min. The results shown in Table 1 indicated that although all reductive sulfur compounds could theoretically provide electrons for the denitrification process, thiosulfate was superior to the other two types from the comprehensive comparison of solubility, the electron availability, the process completion, the stability, as well as the treatment efficiency.

2.2. Selection of carrier

In order to improve the efficiency of the microbial reactors, many researchers tried to immobilize the microorganisms onto the carrier to enrich the functional bacteria and to prevent the sludge washout (Song et al., 2005; Xu et al., 2015).

Table 1 – Comparison of the treatment efficiency of the autotrophic denitrification reactors with different electron donors.

Temperature	10–20°C			Above 20°C		
	L1	L2	L3	L1	L2	L3
Reactor no.						
Electron donor	S	Na_2S	$\text{Na}_2\text{S}_2\text{O}_3$	S	Na_2S	$\text{Na}_2\text{S}_2\text{O}_3$
Average nitrate removal (%)	49.8 ± 10.4	46.7 ± 5.3	92.1 ± 3.1	73.3 ± 14.4	47.5 ± 5.9	99.2 ± 0.5
Average TN removal (%)	40.0 ± 8.9	36.7 ± 5.7	79.9 ± 14.0	72.5 ± 17.3	41.4 ± 7.0	90.0 ± 8.8
Effluent nitrate (mg/L)	5.2 ± 1.2	6.9 ± 0.7	1.0 ± 0.4	2.7 ± 1.7	6.8 ± 0.8	0.01 ± 0.06
Effluent nitrite (mg/L)	2.3 ± 0.5	1.0 ± 0.5	0.39 ± 0.3	0.53 ± 0.14	0.29 ± 0.26	0.08 ± 0.14
The shortest HRT (hr)	4.0	4.0	4.0	2.0	4.0	0.5

HRT: hydraulic retention time; TN: total nitrogen.

Table 2 – Comparison of the denitrification efficiency in the reactors packed with different carriers.

Carrier	Ceramsite	Activated carbon	PWU	No carrier
Average nitrate removal (%)	97.3 ± 4.2	99.7 ± 0.81	80.1 ± 7.8	81.50 ± 14.1
Average TN removal (%)	81.3 ± 16.2	83.4 ± 5.7	75.3 ± 12.6	54.9 ± 18.7
Effluent nitrate (mg/L)	0.60 ± 0.55	0.04 ± 0.10	2.58 ± 1.02	2.47 ± 1.9
Effluent nitrite (mg/L)	0.15 ± 0.24	0.07 ± 0.10	0.29 ± 0.40	1.50 ± 1.05
The shortest HRT (hr)	0.5	1.0	4.0	1.5

PWU: waterborne polyurethane.

Autotrophic bacteria generally have long generation time, and are sensitive to the environmental change. Immobilization was also tried in this study and the immobilization carrier included ceramsite, activated carbon, and waterborne polyurethane (WPU). The average diameter of the ceramsite and activated carbon was about 7 mm and 1–2 mm, respectively. While the WPU was added with seed sludge and then the solidified mixture was cut into 3 × 3 × 3 mm cubic pellets. At the same time, the flocculent sludge system without carrier was also run for comparison.

The four reactors were all kept running at the temperature of 25°C for more than 40 days after start-up. Table 2 shows the denitrification performance of the four systems during the stable running period. The influent nitrate concentration of all reactors was about 13 mg/L.

The ceramsite-packed reactor was started up at the HRT of 6 hr, the average nitrate removal rate was 89% at the beginning. Shortening HRT for the first time greatly affected the denitrification process, but as the time went by this influence had become less and less. The ceramsite system ran stably when the HRT was gradually shortened to 0.5 hr, 97.3% of the nitrate was removed from the nitrate-contaminated water. During the start-up period, the nitrite concentration from this reactor was relatively high, sometimes it reached 2 mg/L. And after the system entered the stable running period, the effluent nitrite decreased to 0.2 mg/L and below.

While using activated carbon as carrier, the nitrate was removed even more completely. The reactor was started up in a few days. Due to the excellent adsorption ability of the activated

carbon, the microorganisms were quickly enriched on the surface or in the pores of the carbon, which could be clearly seen through scanning electronic microscope. Almost 100% of the nitrate was removed, revealing the excellent denitrification performance. However, the demerit of this system was that part of the small granules of the activated carbon could be flushed out when the upflow velocity was over 1 m/hr, thus could cause the system failure. The effluent nitrite from the activated carbon system was very low, almost undetectable. Only when the up-flow rate reached over 1 m/hr and part of the carbon was flushed out, higher nitrite of 0.5 mg/L was detected.

The reactor packed with WPU immobilized sludge showed greater instability comparing with the ceramsite and activated carbon systems. It was also started up at the HRT of 6 hr, and the nitrate removal was 90%. When the HRT was decreased to 4 hr, the nitrate removal decreased to 60% and recovered very slowly. In the next days, gradually shortening HRT to 1.5 hr also caused frequent fluctuation of the denitrification efficiency. During the 45-day-running, the nitrate removal finally stabilized at about 80%. Flowing through the WPU immobilized sludge bed, the treated water contained relatively higher concentration of nitrite, mostly between 1.0 and 3.0 mg/L.

The flocculent sludge system with no carrier was the most unstable one among the four reactors. It started well with nitrate removal of more than 95% at the HRT of 4 hr. However, adjusting the running parameter slightly caused great fluctuation. Even after the HRT was adjusted back to 4 hr or even longer, the unsteadiness still remained. Its treatment ability could not be increased easily. During the 70-day running period, the nitrate removal fluctuated over 60%–95%, with the average value of 80%. And serious nitrite accumulation was found. Most of the time the effluent nitrite was over 1 mg/L, and sometimes it even reached 5 mg/L. The average nitrite reached 1.5 mg/L.

From the comparison of these four reactors, it showed that the autotrophic denitrification process did need the carrier to improve the efficiency. However, different carriers caused very different treatment performance. Activated carbon led to the best denitrification efficiency, yet this kind of carrier was relatively expensive and could not resist the high hydraulic load. Comprehensively considering the denitrification efficiency, the cost and the manipulation convenience, ceramsite could be a good choice.

2.3. Determination of the operational parameters

2.3.1. Seed sludge and start-up

Generally two types of easily available sludge are used as seed sludge for sulfur-based autotrophic denitrification: the excess sludge from activated sludge process, or the anaerobic sludge from sludge digester. In this study, the same amount of

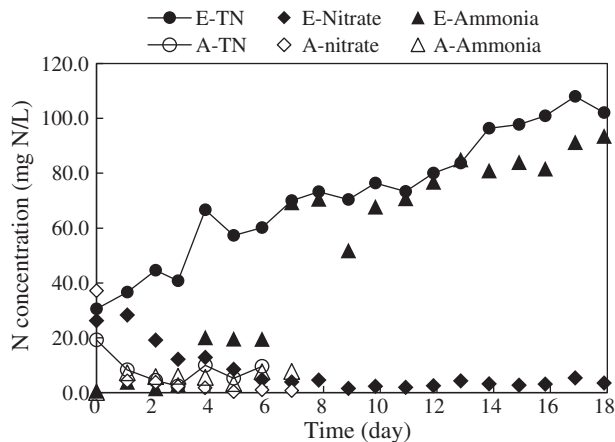


Fig. 2 – Variation of the different types of nitrogen in different seed sludge. “E” represents excess activated sludge and “A” stands for anaerobic sludge.

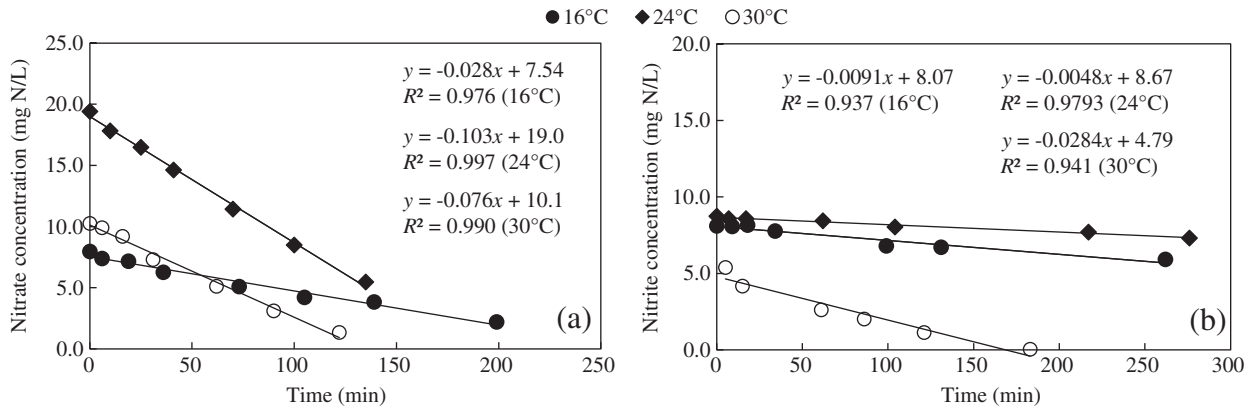


Fig. 3 – Reduction rate of (a) nitrate and (b) nitrite under different temperatures.

aerobic and anaerobic sludge was put into two 2 L cylinders, then submerged in the same amount of 20 mg/L nitrate solution. The cylinders were kept in 25°C incubator and were mixed slightly once every hour to investigate the variation of nitrogen. The experiment was repeated once for the reoccurrence, and Fig. 2 shows the variation of the different types of nitrogen in the centrifuged supernatant.

The TN in the cylinder seeded with anaerobic sludge decreased to 2.36 mg/L, which meant that 90% of the TN was removed within 48 hr. While in the cylinder seeded with excess activated sludge, the TN showed no decrease but continual increase, even after 18 days of incubation.

Although nitrate was reduced swiftly in both cylinders, the variation of ammonia showed very different tendency. Ammonia kept increasing in the excess activated sludge but almost did not change in the anaerobic sludge, which was also the main reason of the great TN difference. The great difference of ammonia variation was probably due to the cell decay and the release of cell materials in the excess sludge, as the excess sludge contained great amount of aerobic and heterotrophic microorganisms which cannot survive without the supply of oxygen and organic substrate.

Obviously, anaerobic sludge was more suitable than the aerobic excess sludge for the seed sludge of autotrophic denitrification. It needed much less time to start up a new

reactor, and avoided the problem of temporary nitrogen increase in the treated water.

2.3.2. Optimal temperature

From the continuous running, obviously, the temperature over 20°C improved the denitrification process a lot. At lower water temperature of 10–20°C, the autotrophic bacteria were of the lower activity and efficiency. Although they still worked, they needed longer HRT to reach the same nitrogen removal. When the water temperature was below 10°C, serious nitrite accumulation occurred, indicating that the nitrite-reducing-bacteria were inhibited first. Then the nitrate removal also turned down, or even ceased when the temperature went down to 6°C and below.

In order to find the optimal temperature for the denitrification process with thiosulfate as electron donor, batch test was performed to investigate the reduction of nitrate and nitrite under different temperatures. As in the natural environment, the temperature of surface water generally varies between 5 and 30°C. Three temperatures, 16, 24, and 30°C, were chosen. Batch test was carried out in six serum bottles packed with the same amount of sludge. Three of them were fed with nitrate substrate and were kept oscillating at 16, 24, and 30°C respectively. The other three were fed with nitrite substrate. The results are shown in Fig. 3.

Fig. 3a shows that when the temperature increased from 16 to 24°C, the reduction rate of nitrate increased very quickly, from 0.028 to 0.103 mg/(L·min). When the temperature increased from 24 to 30°C, the nitrate reduction did not increase but decreased slightly, to 0.076 mg/(L·min). However, Fig. 3b reflected very different changing tendency of nitrite reduction rate. It showed almost no change when the temperature increased from 16 to 24°C, yet a very fast increase was detected when the temperature increased from 24 to 30°C. From these results, it revealed that the nitrate-reducing-bacteria and nitrite-reducing-bacteria have different optimal temperatures. The favorite temperature of nitrate-reducing-bacteria was around 24°C, and the nitrite-reducing-bacteria required 30°C or even higher to reach their activity summit. On the other hand, nitrite reduction was much slower than the nitrate reduction and thus became the bottle neck of the whole process. Combining these two important steps of denitrification, the

Table 3 – The operational parameter of the two reactors of different shapes.

Running stage	Running time (day)	HRT (hr)	HLR (m ³ /(m ² ·hr))	
			L3, flat	L5, slender
A	1–15	4.0	0.13	0.25
B	16–32	2.0	0.25	0.50
C	33–36	1.0	0.50	1.0
D	37–58	0.75	0.67	1.33
E	59–66	0.50	1.0	2.0
F	67–73	0.34	–	3.0
G	74–82	0.29	–	3.5
H	83–91	0.20	–	5.0
I	92–96	0.17	–	6.0

HRT: hydraulic retention time; HLR: hydraulic loading rate.

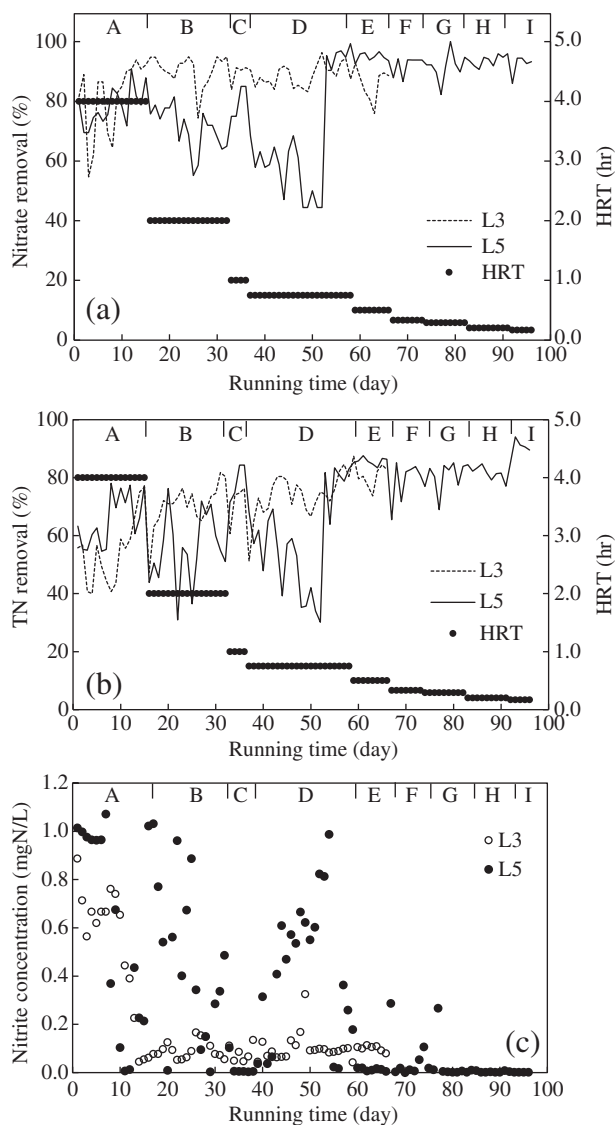


Fig. 4 – Comparison of the treatment performance of the two reactors with different shape (L3: flat; L5: slender reactor). (a) Nitrate removal; (b) TN removal at different HRT; (c) effluent nitrite (A–I represent stage A to stage I, as described in Table 3).

optimal temperature for the whole process should be between 24 and 30°C.

2.3.3. Reactor shape, HRT and hydraulic loading rate

Once the reactor shape is determined, the HRT and the hydraulic loading rate (HLR) are connected by:

$$HLR = (\text{Effective Reactor height})/HRT.$$

When treating a certain amount of nitrate-contaminated water, the reactor volume is determined by HRT, yet the reactor shape could be flat or slender. When the land is limited, the reactor has to develop into the air, a slender

reactor is expected. However, the high HLR caused by a great height may cause the problem of sludge washout, and finally result in the system failure. For this reason, comparison of the reactor shape is necessary. For this purpose, a slender reactor, L5, was set up, with the same volume of 3.0 L, diameter of 62 mm and height of 1 m. Reactor L3 and L5 were both packed with ceramsite, and thiosulfate was used as electron donor, at the S/N ratio (M/M) of 1.0. The tap water in this city, which contained 3–5 mg/L nitrate, was fed as substrate to investigate the influence of HLR on the denitrification of micro-polluted water. Table 3 shows the running parameter of these two reactors and Fig. 4 shows the treatment performance of these two reactors.

As shown Fig. 4a, after start-up, the nitrate removal of the flat reactor (L3) remained stable at about 90% until stage E. In stage E, the HRT was shortened to 0.5 hr and HLR was increased to 1.0 m³/(m²·hr), serious sludge washout was observed and the nitrate removal decreased substantially. But for the slender reactor L5, the nitrate removal performance was lower than L3 in the first stages (stages A–C), and kept going down gradually as the HLR increased (stage D), due to the low biomass, slow growth and greater loss caused by higher up-flow velocity. However, after running for a longer period of time, the nitrate removal showed great improvement by the end of stage D. Later in stage E, L3 running was stopped due to the high SS content in effluent. But L5 was not affected by the high HLR. The nitrate removal remained stable at about 90%, even at the high HLR of 6.0 m³/(m²·hr).

TN removal (Fig. 4b) of the two reactors showed similar tendency. As an important indicator, nitrite in the effluent also revealed the performance of the two reactors. From stage A to stage D, the flat reactor L3 was more stable than L5, with lower nitrite concentration in the effluent. From the end of stage D, the slender reactor started to show superiority. In other words, after the long time of slow biomass accumulation, the slender reactor could stand the high HLR better. This can be explained as follows. First, higher HLR could improve the contact between the substrate and the microorganisms better. Second, higher HLR could flush some old biofilm on the carrier and thus keep the microbial activity. Third, the slender reactor had longer distance for the sludge, gas, and liquor separation, thus could hold more microorganisms and prevent more sludge from washing out.

2.4. Real application for the micro-polluted surface water

2.4.1. Pilot-scale experiment I: up-flow reactor

The pilot-scale experiment was performed at the West Lake, Hangzhou City, China. The West Lake water, which contains the nitrate of 1.5–3 mg N/L, was removed of the suspended solid in a sedimentation tank, then pumped into the denitrification reactor as the raw water. Thiosulfate was added through a dosing pump. The pilot-scale reactor was started up in June, at the HRT of 3 hr, and went on running till the end of November, at the HRT of 30–45 min, according to the temperature. Accordingly, the HLR of the column reactor varied from 1 m³/(m²·hr) to 7 m³/(m²·hr). But due to the typhoon, the salt tide, and the rainstorm, the running had to be intermittent. Fig. 5 shows the water temperature, the operational parameters and the denitrification performance of the pilot study.

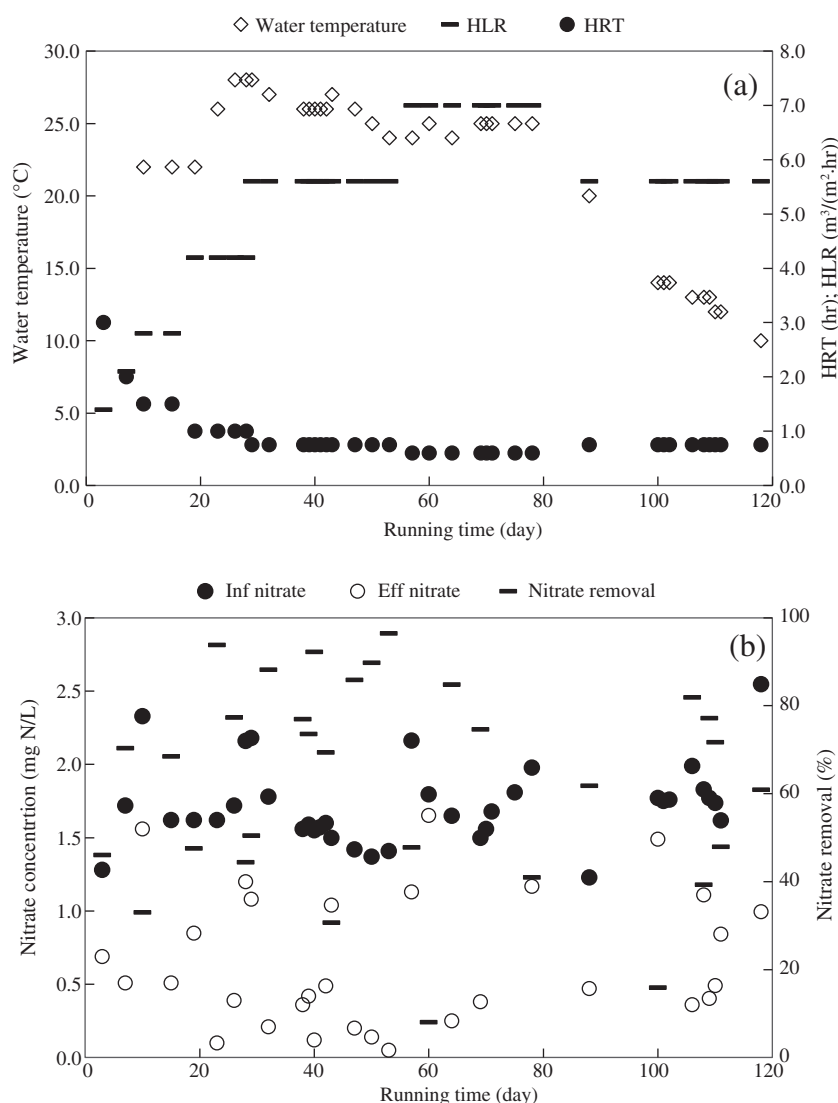


Fig. 5 – The denitrification performance of the pilot-scale reactor I (10 m³/day, up-flow).

Briefly speaking, the pilot-scale experiment was not as stable as the lab-scale one due to the low concentration of raw water and those uncertain factors. When the water temperature was above 20°C, the nitrate removal varied between 70% and 90%, although the HLR reached 7 m³/(m²·hr). Even when the water temperature decreased to 10–15°C, most of the time the nitrate removal could reach 70%. Nitrate removal could be maintained by properly adjusting the HRT. In all, the nitrate removal could ensure the effluent TN no more than 1.5 mg N/L, which is the TN limit for the level IV surface water in China.

However, a new problem has emerged during the pilot-scale study. After 15–20 days of full load operation, the reactor had to be backwashed. After backwashing, it took about 3–4 days to recover. During the recovery period, the effluent quality was not good as the stably running period. This problem has never occurred in the lab-scale study, probably due to the relatively high biomass loss comparing with the reactor volume. It may be solved by modifying the reactor shape, or the running mode, such as adding an expansion part for sludge sedimentation, returning part of the washed-out sludge back into the reactor, or

dividing the big biofilter into more cells but backwashing them in turn.

2.4.2. Pilot-scale experiment II: down-flow reactor

The second pilot-scale reactor was a used, down-flow rectangle biofilter, with the full treatment capacity of 1800 m³/day. This larger reactor ran from April to the end of November. The same source water of West Lake was applied with the influent nitrate varying between 1.0 and 3.0 mg N/L and the HRT from 1 hr to 45 min. As the tank was flat-shaped, the HLR remained 2–3 m³/(m²·hr). The results are shown in Fig. 6.

As shown in Fig. 6, around 80% of the nitrate was removed when the temperature was over 20°C, and when it was lower, the nitrate removal varied between 40% and 80%, indicating the applicability of the process. However, comparing with the pilot-scale experiment I, the treatment performance of the down-flow reactor was worse, and the backwashing period was shorter, about 10 days. The backwashing of the down-flow reactor was more frequent than the up-flow one, obviously the

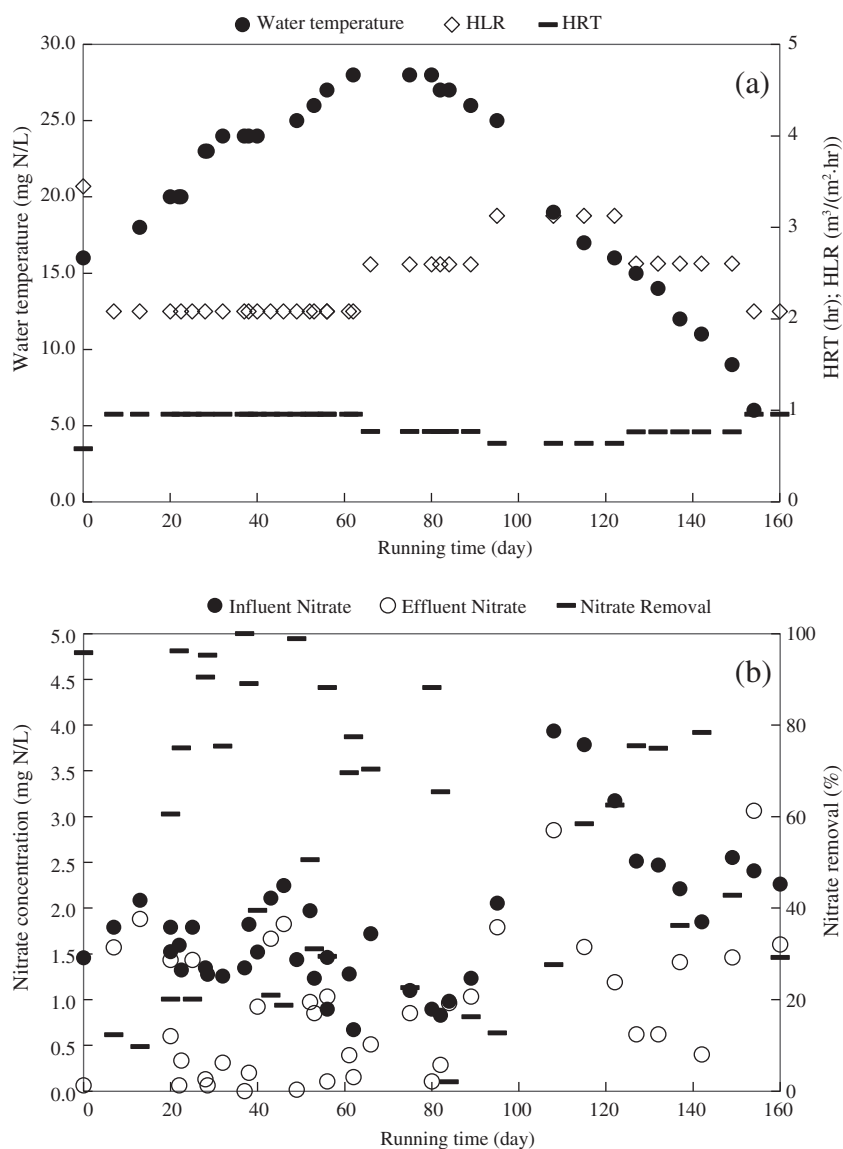


Fig. 6 – The denitrification performance of the pilot-scale reactor II (1800 m³/day, down-flow).

autotrophic bacteria could not grow well enough. This could be explained that in a down-flow filter, the sludge growing on the carrier would soon develop into a scum layer over the surface of the carrier and cause the clogging, so that the reactor had to be backwashed even when the most of the carrier under the top layer were even not utilized. From this viewpoint, the down-flow biofilter was not as efficient as the up-flow one, whether from the running performance or from the management.

Theoretically in the sulfur-based denitrification process, H⁺ is formed and causes pH decrease. So alkalinity supply is important to prevent pH drop. Yet in this study, alkali was added only during the domestication period of the lab-scale experiment using thiosulfate, to adjust pH to 6.5–7.0. After the domestication, alkali was no more added. And in the pilot-scale experiment, no alkali was added even from the beginning. However, both experiments were not affected. It is believed that the reduction of a low concentration of nitrate would not cause a huge pH change and that the microorganisms could adapt themselves to this small-range pH change.

3. Conclusion

Sulfur-based autotrophic denitrification was investigated in the biofilter reactors and the following conclusions are drawn: (1)Thiosulfate was found to be better electron donor than element sulfur and sulfide. Ceramsite was the suitable carrier due to the good denitrification efficiency, low cost and the good resistibility against the high hydraulic loads. (2)Under the optimum conditions, the process could reach a short HRT of 20–30 min and high HLR of 6–7 m³/(m²·hr), and the nitrate removal of more than 80%. (3)Pilot-scale applications on the real micro-polluted lake water were successful.

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