Research Article

Autohydrogenotrophic Denitrification Using the Membrane Biofilm Reactor for Removing Nitrate from High Sulfate Concentration of Water

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This study investigated the performance of an autohydrogenotrophic membrane biofilm reactor (MBfR) to remove nitrate from water with high sulfate concentrations. The results of simulated running showed that TN removal could be over than 98.8% with the maximum denitrification rate of 134.6 g N/m³ d under the conditions of the influent sulfate concentrations of 300 mg SO₄²⁻/l. The distribution ratio of H₂ electron donor for nitrate and sulfate was 70.0 : 26.9 at the high influent loading ratio of sulfate/nitrate of 853.3 g SO₄²⁻/m³ d : 140.5 g N/m³ d, which indicated that denitrification bacteria (DB) were normally dominated to complete H₂ electron with sulfate bacteria (SRB). The results of molecular microbiology analysis showed that the dominated DB were Rhodocyclus and Hydrogenophaga, and the dominated SRB was Desulfohalobium, under the high influent sulfate concentrations.

1. Introduction

Nitrate-contaminated river or groundwater occurred everywhere in the world because the fertilizers were utilized extensively and part of the wastewater from industries was discharged randomly, especially in developing countries [1, 2]. The high concentrations of nitrate in drinking water (>10 mg N/l) would have a high risk to produce nitrosamines and cause methemoglobinemia, which was harmful to people’s health [3, 4]. Therefore, a lot of methods to reduce nitrate from water sources have been reported [5, 6].

The effective methods to reduce nitrate include ion exchange [7] and reverse osmosis [8–10]. Due to the high cost of physiochemical technologies, their applications are limited in some extent [11]. The two normal types of the biological treatment are heterotrophic denitrification and autotrophic denitrification [12, 13]. The cost of the heterotrophic denitrification is high because the organic materials need often to add the carbon source for bacteria in the process which are low in groundwater [14, 15]. There are lots of advantages of autohydrogenotrophic technology, such as clear with hydrogen, low cost, and without secondary pollution [16, 17].

Recently, a new technology of hydrogen- (H₂-) based membrane biofilm reactor (MBfR) has developed and got a good effect, which used autohydrophotropic bacteria in the denitrification processes [16, 18, 19]. The oxidized pollutants, such as SO₄²⁻, CrO₄²⁻, AsO₃⁻, TCE, ClO₄⁻, BrO₃⁻, and SeO₄²⁻, could be reduced by MBfR using H₂ as electron donors [20–23]. While NO₃⁻ and SO₄²⁻ are chemical oxyanions that normally coexist in a variety of waters. There are many reasons caused NO₃⁻ and SO₄²⁻ coexisting in...
water, such as anthropogenic activities related to overusing of fertilizers and wastewater discharges, natural mineralogy related to $\text{SO}_4^{2-}$ minerals, and atmospheric deposition of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ [24]. On the other hand, in MBfR, the autohydrogenotropic bacteria could utilize $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ as electron acceptors to generate energy for their growth [25], and several sulfate-reducing bacteria (SRB) are able to use alternative terminal electron acceptors to reduce sulfate such as nitrate [26].

The following equations could describe the stoichiometry of hydrogenotrophic denitrification and sulfur-reducing:

$$2\text{NO}_3^- + 2\text{H}^+ + 5\text{H}_2 \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$$

$$4\text{H}_2 + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O} + 2\text{OH}^-$$

While in some sites in the world (e.g., natural mineralogy), the contents of sulfate could be as high as hundreds or thousands micrograms per liter in the groundwater, which is used as a drinking water. Because $\text{SO}_4^{2-}$ is not normally considered a health concern, and no MCL has been established for $\text{SO}_4^{2-}$, so many references of autohydrogenotrophic denitrification could concern about sulfate reduction, but the concentrations of $\text{SO}_4^{2-}$ were relatively lower in the in-fluents for research [27].

The aim of this study was to investigate the performance of autohydrogenotrophic denitrification under the high concentrations of sulfate by a hollow fiber membrane bioreactor with polyvinyl chloride (PVC) membrane.

## 2. Materials and Methods

### 2.1. Reactor in the Study.

The theory of denitrification using hydrogenotrophic bacteria is shown in Figure 1(b); the denitrification attached on the outside surface of membrane would utilize the $\text{H}_2$ transferred from the lumen of the membrane at some extent of pressure to accomplish the denitrification. For the reactor, we use a transparent plastic cylinder to hold two membrane modules, and the influent fluid was flowed from upper side to the lower outlet, and the flow rate was controlled by a peristaltic pump (longer BT50-1J, Baoding, PRC), and the membrane made of polyvinyl chloride membrane with hydrophobicity alloy fiber was used in the study. The detailed schematic of the reactor could be seen in Figure 1(a). Also, the parameters of the membrane and the reactor are listed in Table 1.

### 2.2. Influent Water Source and Experimental Conditions.

In the study, the influent water was taken from the sulfate-and nitrate-contaminated groundwater in the vegetable land at the suburb of Qingzhou (Weifang, China), where a lot of fertilizer had been used in the lands. The shallow groundwater around the vegetable land had been contaminated by nitrate and sulfate, and the water quality is shown in Table 2.

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**Table 1: The parameters of the reactor.**

| Parameters                     | Unit | Value     |
|-------------------------------|------|-----------|
| Numbers of fiber module       |      | 2         |
| Outer diameter of fiber       | cm   | 0.15      |
| Inner diameter of fiber       | cm   | 0.085     |
| Fiber number in the reactor   |      | 96        |
| Length of fiber               | mm   | 140       |
| Volume of fibers              | cm$^3$ | 23.74   |
| Available surface area        | cm$^2$ | 633.34  |
| Available volume of reactor   | cm$^3$ | 560      |
| Void ratio                    | %    | 95.76     |
| Specific surface area         | m$^2$/m$^3$ | 113.10 |
| Height                        | cm   | 22.0      |
| Section area of reactor       | cm$^2$ | 28.26   |
| Diameter of reactor           | cm   | 6.0       |
| Available volume of reactor   | cm$^3$ | 560      |

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We started up the reactor by inoculating the biofilm microorganisms from other MBfRs running for hydroge-
nutrophic denitrification for years in our lab. For simulat-
ing the different concentrations of sulfate in the in-
fluent water, some dosage of FeSO$_4$·7H$_2$O was fed in the in-
fluent pumped from the actual groundwater. The detailed exper-
imental design of the reactor running could be seen in
Table 3.

All the fluid samples collected in the experiments were
kept at 4°C until the samples were analyzed. The NO$_3$–N,
NO$_2$–N, and SO$_4^{2−}$ were measured by the ion chromatogra-
phy (Dionex ICS 3000). The H$_2$ unutilized by the denitrifiers
would go into the headspace of the reactor. A GC 14-B
equipped with a TCD detector (Shimadzu Co.) was used
to test the H$_2$ gas concentration in the headspace in the
reactor by pumping gas from the gas port by a syringe,
and the hydrogen content in the liquid could be calculated
by Henry’s law.

2.3. Sampling for Biofilm and the Analysis of Microbiology. In
the experiments, at different running periods for the reactor,
the biofilm would be sampled to analyze the changes of the
microbial communities. For our study, when the water
quality in the effluent was steady, that is, at day 40, day 80,
and day 150, the biofilm samples were collected. According
to our previous research, DNA extractions, PCR, and DGGE
were done; see the detailed methods in [28]. As for the nucle-
otide sequencing, the reamplified DNA products were
analyzed by Sangon Company (Shanghai, China). Shannon-
Wiener index was used to analyze the diversity changes of
microbial communities in different running periods of the
reactor. The relation and the dendrogram generation among

| Table 2: Water quality parameters of the groundwater. |
|-----------------------------------------------|
| Total dissolved solids | pH | Alkalinity (mg/l as CaCO$_3$) | Hardness (mg/l as CaCO$_3$) | DO | Nitrate (mg N/l) | Nitrite (mg N/l) | Sulfate (mg/l) |
|------------------------|----|------------------------------|-----------------------------|----|----------------|----------------|---------------|
| 300–400 | 7.2–7.5 | 320–500 | 400–650 | 6.0–6.4 | 35–60 | ND | 250–450 |
| ND: not detected. |

| Table 3: Experimental design of the reactor running. |
|-----------------------------------------------|
| Running time (day) | Start-up | Run I | Run II | Run III |
|---------------------|---------|-------|--------|---------|
| H$_2$ pressure in the fiber (MPa) | 0.02 | 0.03 | 0.04 | 0.05 |
| Nitrate concentration in the influent (mg N/l) | 10.0 ± 2.0 | 20.0 ± 2.0 | 40.0 ± 4.0 | 50.0 ± 4.0 |
| Sulfate concentration in the influent (mg/l) | 100 ± 10.0 | 200 ± 10.0 | 250 ± 10.0 | 300 ± 10.0 |
| Flow rate (ml/min) | 1.1 | | | |
| HRT (h) | | | | | 8.5 |

![Figure 2: The water quality in the influent and effluent and TN removal.](image)
the biofilm bacteria in different running periods were calculated and analyzed by cluster analysis through the NTSYS-pc (2.10, Exeter Software, USA).

3. Results and Discussion

3.1. Operation and Effluent Quality of MBfR. In the beginning of the experiment, the biofilm established on the out surface of the fiber was only taken 3 days just because of the inoculation of bacteria from the reactors running over than years. Then, the reactor was operated over 155 days to evaluate the performance of MBfR under different conditions. The performance of MBfR over the operation periods was illustrated in Figure 2.

As shown in Figure 2, the influent concentrations of nitrate and sulfate ranged from 10–50 mg N/l and 100–300 mg SO₄²⁻/l through the experiments, respectively. In the whole experiment period, the averages of TN removal were 96.4 ± 2.3%, 98.8 ± 1.0%, and 94.9 ± 2.8% in the Run I, Run II, and Run III, respectively. As for the water quality in the effluent, the averages of nitrate concentrations in the effluents were 0.7, 0.3, and 2.1 NO₃⁻/N mg/l, for Run I, Run II, and Run III, respectively. And for nitrite in the effluent, the contents of nitrite in Run I are not detected, but were 0.2 and 0.4 NO₂⁻/N mg/l, in Run II and Run III, respectively. It suggested that the high concentrations of sulfate have some extent inhabitation to denitrification in MBfR processes.

3.2. Performance of MBfR under High Concentration of Sulfate. In this experiment, the high sulfate concentrations up to 300 mg/l in the influent were used to investigate the performance of MBfR. Under the conditions of the different contents of sulfate in the influent, the denitrification loadings and sulfate loadings could be seen in Table 4.

The volumetric denitrification rates were changed from 55.7 g N/m³ to 134.6 g N/m³ with a good TN removal over than 94.9%, which was mainly caused by increasing the influent nitrate loadings. The sulfate reduction rate was changed from 155.4 to 266.7 g SO₄²⁻/m³, which was not mainly controlled by the influent sulfate loading of 566.3–853.3 g SO₄²⁻/m³, and the average sulfate removals were about 23.5–27.4%. It indicated that the sulfate would be utilized preferentially by denitrification bacteria (DB) than sulfate utilized by SRB in completion with H₂ in MBfR, and nitrate respiration is energetically more favorable than sulfate respiration [31].

In the autohydrogenotrophic denitrification in MBfR, the SRB also utilized hydrogen as electron donor to reduce sulfate to sulfide; therefore, there would be a competition for hydrogen between the reductions of nitrate, sulfate, and other electron acceptors. The distributions of hydrogen electron in electron acceptors at different influent sulfate contents in this study and references are shown in Table 5. The calculations of the hydrogen electron’s distributions in MBfR were according to our previous research [30]. Distributions of hydrogen electron were not only dependent on the concentrations of electron acceptors but also on the types of electron acceptors. But the distribution ratio of H₂ on sulfate would be high as its concentration increases at the same conditions. As for sulfate in this study, even the influent sulfate loading increased

| Table 4: The influent loadings and volume reductions for nitrate and sulfate under different influent sulfate concentrations. |
|-------------------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Influent sulfate contents (mg/l) | Influent sulfate loading (g/m³ d) | Volume sulfate reduction (g/m³ d) | Nitrate loading (g N/m³ d) | Volume denitrification rate (g N/m³ d) | Sulfate in effluent (mg/l) | Nitrate in effluent (mg N/l) | References |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 200 | 566.3 | 155.4 | 57.8 | 55.7 | 145.3 | 0.7 | This study |
| 250 | 707.3 | 166.3 | 112.5 | 111.6 | 191.3 | 0.3 | This study |
| 300 | 853.3 | 226.7 | 140.5 | 134.6 | 221.5 | 2.1 | This study |
| 42 | 118.5 | 50.7 | 56.5 | 55.5 | 24 | 0.3 | [29] |
| 92 | 262.6 | 109.6 | 139.5 | 133.8 | 54 | 2 | [29] |
| 78 | 216.8 | 85.3 | 141.7 | 136 | 46.5 | 2 | [30] |

| Table 5: Distributions of hydrogen electron in electron acceptors at different influent sulfate contents. |
|-------------------------------------------------|----------------|----------------|----------------|----------------|----------------|
| Influent sulfate (mg/l) | Influent nitrate (mg N/l) | Nitrate (%) | Sulfate (%) | Oxygen (%) | Cr (VI) (%) | References |
|------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 200 | 20 | 57.9 | 36.1 | 6.0 | This study |
| 250 | 40 | 71.8 | 24.4 | 3.8 | This study |
| 300 | 50 | 70.0 | 26.9 | 3.1 | This study |
| 42 | 20 | 76.0 | 15.9 | 8.1 | [29] |
| 92 | 50 | 81.2 | 15.2 | 3.6 | [29] |
| 78 | 50 | 87.5 | 12.5 | 0.9 | [30] |
| 78 | 10 | 69.9 | 29.2 | 0.9 | [33] |
| 78 | 5 | 55.7 | 42.8 | 1.5 | [33] |
gradually, the sulfate removal was contained at steady figure of about 25%, while the TN removal was almost over 95%, which can be seen from the distribution of electron-equivalent fluxes that the ratio of nitrate:sulfate was 70.0%:26.9% (Run III). It indicated that DB could get more H2 than SRB whatever of the acceptor influent loading changes. While Table 5 also indicated that the high influent sulfate concentrations or high ratio of influent sulfate concentration to influent nitrate concentration would lead SRB to get more power in the competition for hydrogen among the electron acceptors, which could be used to select the special bacteria in MBfR operations for minimizing sulfate reduction [32].

### Table 6: The H2 utility in the MBfR.

|       | Sum of H2 utility (%) | H2 utility for nitrate (%) | H2 utility for sulfate (%) | H2 utility for O2 (%) |
|-------|-----------------------|----------------------------|----------------------------|-----------------------|
| Run I | 97.7                  | 61.1                       | 36.6                       | 9.3                   |
| Run II| 99.4                  | 75.2                       | 24.2                       | 6.0                   |
| Run III| 99.5                | 73.0                       | 26.6                       | 4.9                   |

The % unutilized hydrogen was calculated according to (2), that is, the part of H2 leaving out of reactor: the part utilized by bacteria. The H2 utility in the reactor is shown in Table 6.

\[
\%H_2\text{unutilized} = 100\times \frac{S_{H,o}}{0.143(S_{3,3} - S_{3,0}) + 0.214(S_{3,1} - S_{3,0} - S_{2,0}) + 0.083(S_{4,3} - S_{4,0}) + 0.125(S_{5,3} - S_{5,0}) + S_{H,o}}, \tag{2}
\]

where the detailed meanings of \(S_{j,i}\), \(S_{3,0}\), \(S_{2,0}\), \(S_{3,1}\), \(S_{4,0}\), and \(S_{H,o}\) could be seen in [30].

As shown in Table 6, the sum of hydrogen utilization efficiency over the 3 periods was 97.7–99.5%; the remains may go into the effluent or out of the water. Among the sum of the H2 utility, nitrate got much more quota than that of sulfate and oxygen.

### 3.4. Analyses of Microbial Community.

The microbial communities in each running period of the reactor could be seen in the analyses of the DGGE (Figure 3). The DGGE indicted the dominant bands. Even the operation period was long in each running stage with different concentrations of sulfate in the influent, while the autohydrogenotrophic bacteria growth was very slow and the change of microbial community was considerably slow. In the beginning period of Run I, the bands were not clear and complicated, which indicated that the biofilm needs acclimation furthermore. While several bands, which were clear and simple, could be seen in Run II and Run III. The special bands with number 2, 3, and 4 in DGGE which were dominated were cut and sent to be sequenced. The results indicated that the bacteria in bands 2, 3, and 4 were similar to Rhodocyclus, Hydrogenophaga, and Desulfohalobium, with the similarity of 99%, 98%, and 99%, respectively. The Rhodocyclus and Hydrogenophaga were normal autotrophic bacteria, belonging to beta divisions within the Proteobacteria. This is consistent with our previous study [28]. The Desulfohalobium was found in Runs II and III, which is a Gram negative, anaerobic, sulfate-reducing, moderately halophilic, and rod-shaped bacterial genus from the family of Desulfovibrionaceae. This indicated that the SRB could be abundant with the influent concentration increasing and could enhance its strength of competition with nitrate for H2 [31].

### 4. Conclusion

The study investigated the performance of MBfR to remove nitrate companied with high influent concentrations of sulfate over 155 days. The results indicated that even in high concentration of sulfate in influent, the MBfR also could get a good denitrification effect with nitrate and nitrite under the US standard. The analysis of the molecular microbiology showed that microbial community structures of Runs II and III were similar, simple, and stable. The bacteria species of Betaproteobacteria which include Rhodocyclales and Hydrogenophaga were dominant DB for nitrate removal. The Desulfohalobium was found to be a dominant SRB in Runs II and III under the high concentrations of sulfate. The results would give some directions on the actual application of MBfR to remove nitrate or other oxidations in the drinking water.

![Figure 3: DGGE and on the day 40 (S1), day 80 (S2), and day 150 (S3) (the Arabic numerals meant the different dominated bands in the operation of MBfR).](image-url)
Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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