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A novel CSTR-type of hollow fiber membrane biofilm reactor for consecutive nitrification and denitrification

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Abstract

A continuous stirred tank reactor (CSTR) type of hollow fiber membrane biofilm reactor (HF-MBfR) using composite membranes was investigated for the nitrogen removal in synthetic wastewater. The CSTR-type of HF-MBfR process couples autotrophic biological nitrogen removal reactors with the bubbleless mass transfer of oxygen and hydrogen through hollow fiber membranes. For nitrification, CSTR-type of HF-MBfR was operated over 400 days and for hydrogenotrophic denitrification, CSTR-type of HF-MBfR was operated over 300 days. The maximum steady-state NH_4^+-N removal rate achieved was 0.25 kg N/m^3 day (2.06 g N/m^2 day) and the denitrification rate achieved was 0.22 kg N/m^3 day (1.72 g N/m^2 day). Consequently, in the HF-MBfRs, biofilms were formed stably on surface of membranes, and nitrification and hydrogenotrophic denitrification were performed successfully during long-term operation.

Keywords: CSTR-type of HF-MBfR; Nitrification; Hydrogenotrophic denitrification

1. Introduction

Nitrification and denitrification are two main steps in removal of nitrogenous compounds from groundwater and wastewater. Nitrification process involves the two-step conversion of ammonia to nitrite and nitrite to nitrate by autotrophic bacteria, *Nitrosomonas* and *Nitrobacter* species. Denitrification process comprises heterotrophic denitrification and autotrophic denitrification. Heterotrophic denitrification, widely used in nitrogen removal process, is considered as an efficient denitrification process in nitrate removal if C/N ratio of raw wastewater is high. However,

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heterotrophic denitrification requires an addition of external organic carbon to supply electron donor in ground water or some industrial wastewater which has insufficient biodegradable organic carbon as the electron donor.

Autotrophic denitrification has developed recently because of these advantages: (1) only inorganic carbon is used [1], which reduces the risk of organic residues and (2) biomass yields are low. There are four biological process of autotrophic denitrification [2]: hydrogen oxidizing denitrification, reduced sulfur oxidizing denitrification, ferrous iron oxidizing denitrification, and chloric compound oxidizing denitrification. In hydrogen oxidizing denitrification, hydrogen is used as an electron donor and energy source and this process offers these advantages: (1) residual hydrogen that remains in water is harmless and does not interfere with subsequent water treatment and (2) reaction byproducts are harmless [3]. However, since hydrogen has low solubility in water and is an explosive compound if it supplies to excessive amounts, autotrophic denitrification using hydrogen gas has not been popular technology for nitrate removal in industrial wastewater and groundwater containing low concentration of available organic compounds.

A membrane-attached biofilm reactor (MABR) is a biofilm process in which oxygen as an electron acceptor or hydrogen as an electron donor is supplied directly to biofilm formed on a membrane by bubbleless membrane dissolution. Due to bubbleless gas mass transfer, favorable design and the operational features of the MABR process it has been hypothesised that close to 100% gas utilization efficiency is achievable for biological wastewater treatment [4]. Therefore, MABR overcomes the explosion hazard of conventional gas transfer and minimizes the cost of supplying gas as the electron acceptor and donor. A hollow fiber membrane biofilm reactor (HF-MBfR) in which gas mass transfer is achieved using hollow fiber membranes, provide a high surface area for biofilm formation. While many studies have been published on using tubular type and a single membrane biofilm reactor for aerobic or anaerobic operation [5–8], there is little information about other reactor types, combined membrane biofilm reactors for total nitrogen treatment in wastewater. The purpose of this study is to investigate the performance of nitrogen removal using autotrophic bacteria in a continuous stirred tank reactor (CSTR) type of HF-MBfR using composite membranes. The membrane biofilm reactor of tubular type uses circulation pumps to generate a completely mixed state on the membrane surface [9]. This reactor type requires about ten times higher than the feed flow rate to maintain a completely mixed state. In CSTR-type of HF-MBfR, a completely mixed state on the membrane surface is generated by rotating impellers set in the bottom of reactor. Therefore, it does not need a circulation pump and an existing wastewater treatment system can be used by adding membrane units into the biotreatment reactor.

2. Materials and methods

2.1. Experimental system

The schematic diagram of the CSTR-type of HF-MBfR system is showed in Fig. 1. The treatment system consisted of a nitrification reactor (R1) for ammonium oxidation and a denitrification reactor (R2) for removal of the oxidized nitrogen. A transparent acrylic cylinder tank was used as a hollow fiber membrane reactor, in which four membrane modules were directly submerged. The hollow fiber membrane reactors had a height of 40 cm and a diameter of 16 cm. A completely mixed state on the membrane surface was generated by a magnetic stirrer set in the bottom of reactor. The gas permeable hollow fibers were manufactured by Mitsubishi Rayon (Model MHF 200TL, Japan) and are a multi-layered composite fiber. The wall of the fiber is made up of two different materials. The outer and inner layers of the fiber wall are composed as microporous polyethylene. Between the two layers is an ultra-thin layer

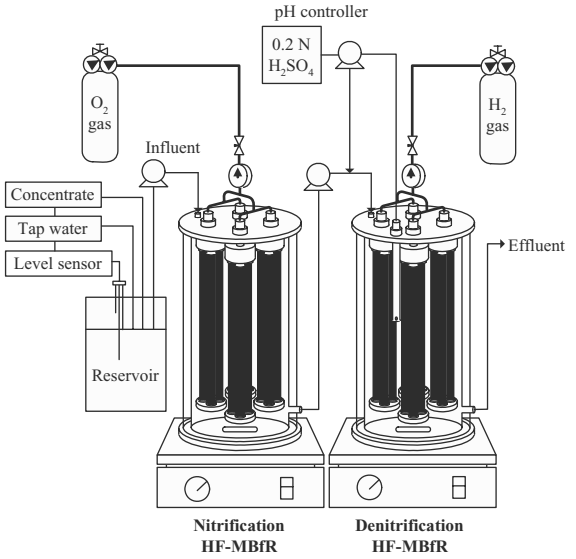

Fig. 1. Schematic diagram of the CSTR-type hollow fiber biofilm reactor.

of non-porous polyurethane. This non-porous layer allows the creation of a high driving force for gas dissolution without bubble formation. The inside and outside diameters of a hollow fiber are 0.0135 cm and 0.027 cm, respectively.

The membrane module consisted of three individually potted bundles of polyethylene hollow fiber membranes. Each hollow fiber bundle contained 320 fibers. The ends of each fiber bundle were potted into a 10 mm OD × 20 mm cylindrical plug of polyurethane. The fiber bundles had 250 mm of active length to yield a specific area of 148 m^2/m^3 and provides 679 cm^2 of membrane surface area. The four membrane modules in each reactor provide 8143 cm^2 of membrane surface area with 3840 hollow fibers. The void ratio of the working reactor volume (volume of the reactor was 6554 cm^3; volume of fiber was 54 cm^3) was 99.2% when the hollow fibers were free of biofilm. Oxygen and hydrogen were supplied to the lumen side of the fibers from a pressurized gas tank via a metering valve (Parker, USA).

2.2. Experimental conditions

Concentrated synthetic wastewater was fed by a piston pump (FMI LAB PUMP, Model QSY, USA) into a reservoir. Tap water without synthetic wastewater was also supplied into the reservoir to dilute the concentrate, being controlled through a level sensor set inside the reservoir so that the concentrate of wastewater was kept constantly. The diluted synthetic wastewater was supplied to the hollow fiber membrane reactor by a peristaltic pump (Masterflex Cole-Parmer, USA) and the flow rate of influent was changed according to hydraulic retention time (HRTs) during the experimental period.

In R1 and R2, $NaHCO_3$ was used as an inorganic carbon source for the growth of autotrophic microorganisms and for the prevention of pH drop for nitrification, and $(NH_4)_2SO_4$ was used as a nitrogen source in R1. For the experiment in R2, $NaNO_3$ was used as nitrogen source and a phosphate buffer (K_2HPO_4 + KH_2PO_4) and H_2SO_4 (0.2 N) were used to prevent pH rise for denitrification. In R2, the phosphate buffer was added in the raw synthetic wastewater from 65 day to 205 day. During the operation period except from 65 day to 205 day, pH was controlled by an auto controller in R2. When pH rose to 8, 0.2 N H_2SO_4 was added automatically in R2.

By changing a volumetric influent loading rate as NH_4^+-N and NO_3^--N, the performance of the reactors was estimated (Table 1). The activated sludge from a municipal wastewater treatment plant was inoculated into R1, and the anaerobic sludge taken from a sludge digester at the same plant was inoculated into R2.

2.3. Analytical methods

All samples of each reactor were kept in the refrigerator at 4°C until analysis and analyzed within 2 days after sampling. NO_2^--N and NO_3^--N concentrations were determined by Ion Chromatography (DX-120, Dionex Inc.) and NH_4^+-N concentration was analyzed using Kjeldahl analyzer

Table 1
Experimental conditions

	R1					
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Term (day)	0–67	68–126	127–175	176–256	257–361	362–403
HRT (h)	12	10	8	7	6	5
Nitrogen (mg N/L)	50	50	50	50	50	50
	R2					
	Run 1	Run 2	Run 3	Run 4	Run 5	
Term (day)	0–39	40–98	99–171	172–217	218–298	
HRT (h)	12	10	8	7	6	
Nitrogen (mg N/L)	50	50	50	50	50	

(KJELTEC 1035 Analyzers). Alkalinity was measured according to Standard Methods [10].

3. Results and discussion

3.1. Nitrification performance in R1

Figs. 2 and 3 show the changes of NH_4^+-N, NO_2^--N, and NO_3^--N concentrations in R1 during operation period. The nitrification HF-MBfR (R1) was continuously operated for 403 days. NH_4^+-N concentration of influent was 50.5 ± 3.8 mg N/L. Start-up of R1 was initiated by seeding with 200 mL of activated sludge achieved from a municipal wastewater treatment plant. Synthetic wastewater and the bacterial seed were recirculated through R1 to allow the biofilm growth on the membrane surface for 2 days. During the start-up period, biofilm formation on the hollow fiber membranes was very slow, and

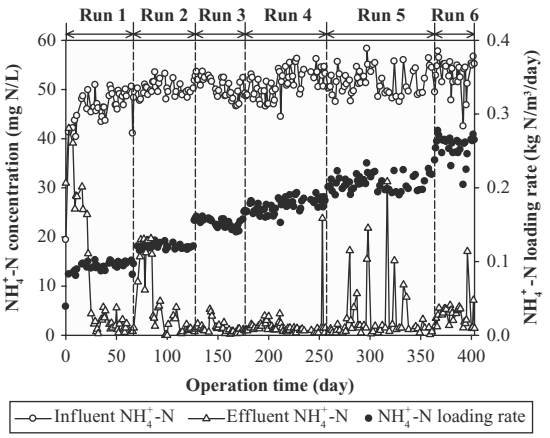

Fig. 2. Variations of NH_4^+-N concentration and loading rate in R1.

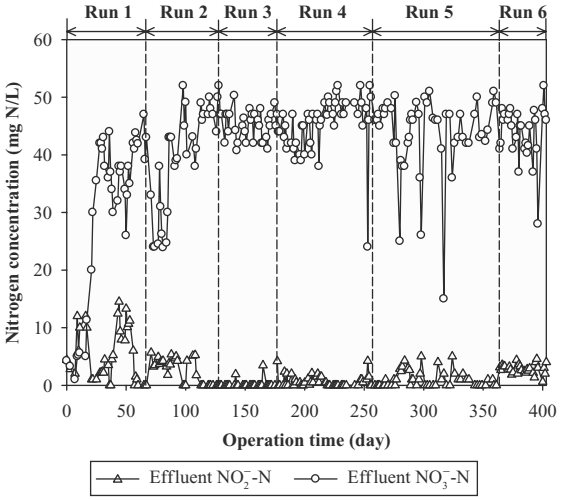

Fig. 3. Variations of effluent NO_2^--N and NO_3^--N concentrations in R1.

bacterial distribution on the membrane was not completely homogenous along the length of the fibers. The removal of influent NH_4^+-N and oxidation to NO_3^--N were almost complete occurred when the nitrification HF-MBfR was operated continuously (12 h HRT, NH_4^+-N loading rate 0.10 kg N/m^3 day) after 25 day during Run 1. After then, though NO_2^--N concentration of effluent increased to 14.5 mg N/L on 44 day, the complete oxidation of NH_4^+-N in influent was recovered after 56 day. From 68 day onward NH_4^+-N loading rate was increased gradually from approximately 0.12 to 0.24 kg N/m^3·day by reducing HRT from 10 to 5 h.

During Run 2, NH_4^+-N concentration of effluent increased to 19.7 mg N/L and nitrite build-up was observed due to increasing loading, however, NH_4^+-N concentration of effluent decreased gradually after 109 day. In Run 4 and Run 5, the intermittently high NH_4^+-N concentrations of effluent were caused by faults of mixing by the magnetic stirrer. Except for the results obtained in these unstable operation periods, the average concentrations of effluent were 1.0 ± 0.6 mg N/L, 1.5 ± 1.2 mg N/L, 1.5 ± 0.9 mg N/L and 1.3 ± 0.8 mg N/L in steady-state from 109 to 361 day. The average NO_2^--N concentrations of effluent were less than 1.0 mg N/L and nitrite build-up was not observed during this period. The average NO_3^--N concentration was 92 ± 5% of the removed NH_4^+-N concentration in R1. In Run 6 (5 h HRT, NH_4^+-N loading rate 0.24 kg N/m^3 day), from 362 to 403 day, NH_4^+-N concentrations of effluent increased slightly and the average concentration of effluent was 3.9 ± 1.7 mg N/L. As shown in Fig. 3, not all NH_4^+-N of influent was oxidized to NO_3^--N. During this period, the average NO_3^--N concentration was 90.1 ± 4.4% of the removed NH_4^+-N concentration in R1 and the average NO_2^--N concentration was 2.8 ± 0.9 mg N/L. As shown in this result, in Run 6, the nitrification capacity of the reactor used in this study reached its limit.

From Run 2 to Run 6, NH_4^+-N volumetric loading rate was increased from 120.8 to 255.3 g N/m^3 day (Table 2). The average volumetric NH_4^+-N removal rates were 114.9, 147.3, 170.2, 197.8 and 236.5 g N/m^3 d in the steady-state and the average NH_4^+-N removal efficiency was above 95% all through the Run except for Run 6. The NH_4^+-N specific surface loading rate was increased gradually from 0.96 to 2.04 g N/m^2 day. In R1, the average specific NH_4^+-N removal rates were 0.92, 1.18, 1.36, 1.58 and 1.89 g N/m^2 day (Table 3). The maximum steady-state volumetric NH_4^+-N removal rate was 258.6 g N/m^3 day, which corresponded to a membrane specific NH_4^+-N removal rate of 2.06 g N/m^2 d.

3.2. Hydrogenotrophic denitrification performance in R2

Fig. 4 shows the changes of NO_2^--N and NO_3^--N concentrations in R2. The denitrification HF-MBfR (R2) was operated for 302 days continuously. NO_3^--N concentration of influent

Table 2
NH_4^+-N loading rates and removal rates in R1

	Day	No. of samples	Volumetric influent loading rate (g N/m^3 day)	Volumetric removal rate (g N/m^3 day)	NH_4^+-N removal rate (%)
Run 2	68–126	21	120.8 ± 3.8	114.9 ± 5.7	95.1 ± 4.3
Run 3	127–175	33	151.8 ± 6.2	147.3 ± 5.9	97.1 ± 2.2
Run 4	176–256	52	175.4 ± 9.7	170.2 ± 10.7	97.0 ± 1.7
Run 5	257–361	46	205.5 ± 10.1	197.8 ± 11.8	96.3 ± 4.0
Run 6	362–403	28	255.3 ± 15.8	236.5 ± 15.4	92.7 ± 3.0

Table 3
Specific NH_4^+-N membrane surface loading rates and removal rates in R1

	Day	No. of samples	Specific influent loading rate (g N/m^2 day)	Specific removal rate (g N/m^2 day)
Run 2	68–126	21	0.96 ± 0.03	0.92 ± 0.05
Run 3	127–175	33	1.21 ± 0.05	1.18 ± 0.05
Run 4	176–256	52	1.40 ± 0.08	1.36 ± 0.09
Run 5	257–361	46	1.64 ± 0.08	1.58 ± 0.10
Run 6	362–403	28	2.04 ± 0.13	1.89 ± 0.12

was 51 ± 2.9 mg N/L. Anaerobic sludge was inoculated in the start-up period of R2 which was achieved from a sludge digester at a municipal wastewater treatment plant. Synthetic wastewater added $NaNO_3$ as a nitrogen substrate and the bacterial seed were recirculated through R2 to allow the biofilm growth on the membrane surface for 2 days. During the start-up period biofilm formation on the hollow fiber membranes was slightly faster than R1. About 90% denitrification rate was accomplished when the denitrification HF-MBfR was operated continuously (12 h HRT, NO_3^--N loading rate 0.1 kg N/m^3 day) after 20 day in Run 1. Though NO_2^--N concentration of effluent was accumulated to 49.0 mg N/L on 11 day, with a corresponding decrease in NO_2^--N of effluent, NO_2^--N of effluent was not detected after 30 day. From 40 day onward NO_3^--N loading rate was increased gradually from approximately 0.12 to 0.20 kg N/m^3 day by reducing HRT from 10 to 6 h.

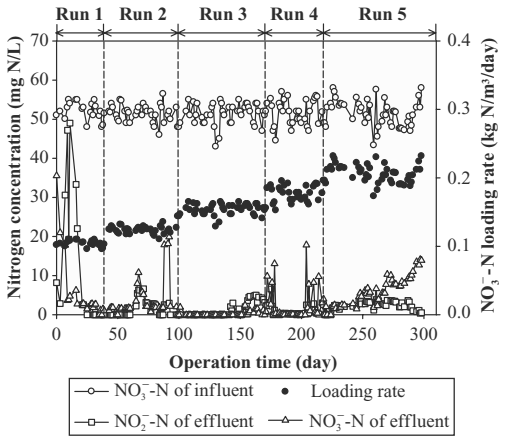

Fig. 4. Variations of NO_2^--N and NO_3^--N concentrations in R2.

The performance of R2 was very good, from 43 to 60 day, at a HRT of 10 h, with NO_3^--N concentrations of effluent were maintained below 2.0 mg/L and NO_2^--N was not detected in this period. As shown in Fig. 4, NO_2^--N and NO_3^--N concentrations were increased gradually, therefore, the denitrification rate decreased to 74%. From the start-up period to 66 day, H_2 partial pressure was maintained at 4 psi. For increasing H_2 flux, H_2 partial pressure was increased gradually to 10 psi, however, the denitrification rate decreased to 68%. At 67 day, the membrane modules were picked up in the reactor, and then, had soaked and shake smoothly in tap water to remove biofilm that grows excess. After then, the denitrification rate was recovered to 97%. It was suggested that the hydrogen mass transfer was limited by the biofilm thickness. During the experiment period, excess biofilm was removed three times on 67, 163 and 240 day. In Run 2 and Run 4, the intermittently high NO_3^--N concentrations of effluent were caused by faults of mixing by the magnetic stirrer.

Except for the results obtained in these unstable operating periods, the average NO_3^--N concentrations of effluent were 1.6 ± 0.6 mg N/L, 0.2 ± 0.5 mg N/L and 0.2 ± 0.3 mg N/L in the steady-state. And, the average NO_2^--N concentrations

Table 4
NO_3^--N loading rates and denitrification rates in R2

	Day	No. of samples	Volumetric influent loading rate (g N/m^3 day)	Volumetric denitrification rate (g N/m^3 day)	Denitrification rate (%)
Run 2	40–98	27	123.9 ± 8.2	118.4 ± 7.1	95.6 ± 2.9
Run 3	99–171	42	153.8 ± 8.2	150.2 ± 9.0	97.7 ± 3.5
Run 4	172–217	22	177.3 ± 11.6	175.3 ± 11.2	98.9 ± 1.4
Run 5	218–298	50	206.2 ± 13.5	173.1 ± 21.6	83.8 ± 8.0

Table 5
Specific NO_3^--N membrane surface loading rates and denitrification rates in R2

	Day	No. of samples	Specific influent loading rate (g N/m^2 day)	Specific denitrification rate (g N/m^3 day)
Run 2	40–98	27	0.99 ± 0.04	0.95 ± 0.06
Run 3	99–171	42	1.23 ± 0.07	1.20 ± 0.07
Run 4	172–217	22	1.42 ± 0.09	1.40 ± 0.09
Run 5	218–298	50	1.65 ± 0.11	1.38 ± 0.17

of effluent were 0.7 ± 1.2 mg N/L, 0.9 ± 1.5 mg N/L and 0.4 ± 0.5 mg N/L in the steady-state. During Run 5 (6 h HRT, NO_3^--N loading rate 0.20 kg N/m^3 day), from 218 to 298 day, NO_3^--N concentrations of effluent increased slightly and the average concentration of effluent was 6.0 ± 3.8 mg N/L. In this period, the average denitrification rate was 83.8 ± 8.0% in R2 and the average NO_2^--N concentration was 2.3 ± 1.1 mg N/L. As shown in this result, in Run 5, the denitrification capacity of the reactor reached its limit.

From Run 2 to Run 5, NO_3^--N volumetric loading rate was increased from 123.9 to 206.2 g N/m^3 day (Table 4). The average volumetric denitrification rates were 118.4, 150.2, 175.3 and 173.1 g N/m^3 d in steady-state and the average denitrification rate was above 95% all through the Run except for Run 6. The NO_3^--N specific surface loading rate was increased gradually from 0.99 to 1.65 g N/m^2 day. In R2, the average specific denitrification removal rates were 0.95, 1.20, 1.40 and 1.38 g N/m^2 day (Table 5). The maximum steady-state volumetric denitrification rate achieved was 216.6 g N/m^3 day, which corresponded to a membrane specific denitrification rate of 1.72 g N/m^2 day.

4. Conclusions

In this study, by changing a volumetric influent loading rate as NH_4^+-N and NO_3^--N, nitrogen removal of synthetic wastewater in the absence of organic carbon was evaluated using CSTR-type of HF-MBfR system. The CSTR-type of HF-MBfR contained composite membranes which provide 124 m^2/m^3 of the specific membrane surface area, and occupied 0.8% of the reactor volume. The nitrification CSTR type of HF-MBfR was operated over 400 day. The maximum steady-state volumetric NH_4^+-N removal rate achieved was 0.25 kg N/m^3 day, which corresponded to the membrane specific NH_4^+-N removal rate of 2.06 g N/m^2 day. The denitrification CSTR-type

of HF-MBfR was operated over 300 days. The maximum steady-state volumetric denitrification rate achieved was 0.22 kg N/m^3 day, which corresponded to the membrane specific denitrification rate of 1.72 g N/m^2 day. High rates of nitrification and denitrification are achieved by providing slow growing bacteria like as nitrifying bacteria and hydrogenotrophic denitrifying bacteria, large surface area for biofilm attachment. Hollow fiber membranes provide a large surface area for gas transfer and biofilm attachment while occupying a relatively small volume within the bioreactor. Therefore, the high volumetric nitrogen removal rates can be achieved by addition more hollow fibers.

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