Performance and membrane foulant in the pilot operation of a novel biofilm-membrane reactor

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Abstract We have developed a novel biofilm-membrane reactor (BMR) in which a nitrifying biofilm is fixed on the surface of a rotating membrane disk. With this reactor, both strict solid-liquid separation and oxidation of ammonia nitrogen can be simultaneously performed. Based on the results obtained in previous bench-scale experiments, a pilot-scale study was conducted using river water at a water purification plant. The results obtained in the pilot study can be summarized as follows. (1) By implementation of pre-treatment (coagulation and sedimentation) and simple membrane cleaning (sponge cleaning), the filter run could be continued for 17 months without any chemical washing. (2) Sufficient nitrification was observed when water temperature was high. Deterioration in nitrification efficiency during winter was reduced by the addition of phosphorus. (3) In addition to nitrification, biological oxidation of AOC and manganese can be expected with the BMR. In this study, both AOC and manganese concentration in the permeate decreased to a level less than 10 µg/L. (4) Irreversible membrane fouling, which was thought to be mainly caused by manganese, became significant as the operation period became longer.

Keywords Biofilm-membrane reactor; biological nitrification; drinking water treatment; membrane fouling

Introduction
The use of membranes for treatment of drinking water has received much attention recently because of the ability of membranes to remove human pathogens, including Cryptosporidium and Giardia, which are resistant to chlorine disinfection. However, membranes cannot efficiently remove ammonia nitrogen (NH₄⁺-N), which causes the increase of chlorine demand and may promote the formation of disinfection by-products (DBPs) such as trihalomethane (THM). In addition, NH₄⁺-N reacts with chlorine to produce chloramines, which causes a deterioration in the taste of tap water. In order to overcome these problems, we have proposed a novel membrane process in which a nitrifying biofilm is fixed on the surface of a rotating membrane disk. Figure 1 shows the concept of the novel biofilm-membrane reactor (BMR). With this reactor, both strict solid-liquid separation and oxidation of NH₄⁺-N can be simultaneously performed. We have carried out experiments in the laboratory using a bench-scale equipment, and the experimental results indicated that this is a feasible process (Kimura et al., 2000, 2001). Based on the results obtained in those experiments, a pilot scale study was conducted using river water at an existing water purification plant. In the present study, the performance and fouling of the membrane during long-term (about 17 months) operation were examined.

Materials and methods
Characteristics of raw water
A pilot study was conducted at Kami-Ebetsu Water Purification Plant in Ebetsu City, located 20 km northeast of Sapporo, Japan. The plant draws water from Chitose River. This river runs through cities, farming areas and peat bog areas before reaching the treatment plant. There are also several wastewater treatment facilities upstream of the plant. As a result, the water is severely polluted before it reaches the water intake point. Throughout
the year, the raw water contains a considerable amount of organic substances (up to 10 mg DOC/L). The fluctuation of turbidity in the raw water is substantial, from 5 turbidity units (TU) to 300 TU. The water temperature decreases to a low level in winter (around 1°C), resulting in relatively high concentrations of NH₄⁺-N and manganese in the water during winter.

Experimental apparatus
A pilot-scale rotating membrane disk module was installed at Kami-Ebetsu Water Treatment Plant. Figure 2 shows the water collection mechanism of the rotating membrane disk. Figure 3 shows a flowchart of the pilot experiment. The module characteristics employed in this study are as follows: working volume of the membrane chamber, 300 litres; membrane diameter, 750 mm; number of membrane disks, 6; and total membrane area, 4.5 m². The membrane is made from polysulfone and has a cut-off molecular weight of 750,000 Da. One part of each membrane disk was always above the water surface during the filter run. This membrane module is commercially available (Hitachi Plant & Construction, Tokyo, Japan) and has already been used in full-scale night soil treatment plants for solid-liquid separation. Coagulation with poly-aluminium chloride and flocculation/sedimentation in a Jet Mixed Separator (JMS) (Watanabe et al., 1998) were carried out.

Experimental conditions
Poly-aluminium chloride was dosed at a concentration of 5–10 mg as Al/L, and NaOH was dosed to control the pH of coagulated water within the range of 6.5–7.5. The plant was always operated with overflow from the membrane chamber, resulting in a water recovery ratio, defined as \( \frac{Q_p}{Q_{in}} \), in the range of 0.9–0.95. Intermittent operation (30 minutes of
filtration and 2 minutes pause) was also carried out. The membrane flux was set at various values as shown in Figure 4. The rotational speed of the disks was fixed at 10 rpm. Prior to the continuous filter run, microorganisms were seeded in the membrane chamber. The microorganisms were collected from a biofilter installed at the same plant, in which active nitrification was observed. Dead-end filtration was carried out in order to fix the microorganisms on the membrane surface.

**Sponge cleaning**

“Sponge cleaning” was carried out five times during the pilot filter run. The procedure for “sponge cleaning” was as follows. The suction pump was stopped, and sponge cubes were placed in the membrane chamber. The overflow valve was then closed to rise the water surface level to a level sufficient for submergence of the membrane disks, and the rotational speed of each disk was increased from the normal speed of 10 rpm to 70 rpm. After 1 hour, the sponge cubes and detached cake were drained. The operation was then re-started.

The sponge cubes used for cleaning were made by cutting dishwashing sponge into approximately 1 cm cubes. The total volume of the sponge cubes placed in the chamber was approximately 2,000 ml.

**Analytical methods**

The concentrations of ammonia, humic substances (expressed by UV absorbance at 260 nm) and turbidity were measured at the plant as soon as samples were taken. Metal samples were preserved with 0.1 N HNO₃, and measurements in metal samples were carried out using graphite furnace atomic absorption spectrometry (Hitachi Z-5700). Concentrations of assimilable organic carbon (AOC) were measured by the procedure described by van der Kooij et al. (1982).

**Results and discussion**

**Increase in membrane filtration resistance**

After fixation of the biomass, the continuous filter run was started on January 21, 1999. Figure 5 shows change in the membrane filtration resistance, calculated by the following equation:

$$ R = \frac{\Delta P}{\mu J} $$

where $R$ is the filtration resistance ($m^{-1}$), $\Delta P$ is the transmembrane pressure (Pa), $\mu$ is the water viscosity (Pa•s) and $J$ is the membrane flux ($m^2s^{-1}$). In Figure 5, the data were adjusted to 20°C equivalent values. The filtration resistance increased gradually, and the operation could be continued for more than 4 months at the membrane flux of 0.5 m/d. The first sponge cleaning was carried out on May 10, 1999. This sponge cleaning was found to be
very effective in removing accumulated cake. The operation was re-started after draining the sponge cubes and detached cake. The filtration resistance increased very rapidly after the first cleaning because water with high turbidity was fed to the membrane chamber due to a failure in the pre-treatment (data not shown). As a result of the rapid increase in the filtration resistance, the second sponge cleaning had to be conducted within 1 month after the first one. After the second cleaning, the operation could be continued stably even at the membrane flux of 0.8 m/d, which was the highest flux used in this study. The third cleaning was carried out on October 19, 1999 and was effective in reducing the resistance. The rate of increase in resistance was higher after than before the third cleaning. The reason for this difference is not clear, but it may be related to some microbial activity on the membrane surface. The water temperature dropped rapidly in the same period, which might reduce the microbial activity that maintained the higher membrane permeability. To continue the operation at a high membrane flux, another sponge cleaning should have been carried out. However, another cleaning was not carried out because it was expected to cause severe deterioration in biological treatment efficiency (detailed description given later). Therefore, the membrane flux was set at a lower value to continue the operation. As a result, the rate of increase in resistance was lowered. The fourth sponge cleaning was carried out after a 6-months interval, on April 22, 2000. This sponge cleaning was not as effective in reducing filtration resistance as the previous cleanings. The fifth cleaning, carried out 43 days after the fourth cleaning, did not greatly improve membrane permeability. These results indicate that the dominant membrane fouling mechanism at the times of the fourth and fifth cleanings was different from that at the times of the previous cleanings; i.e. irreversible filtration resistance was significant at the times of the fourth and fifth cleanings, while cake resistance (reversible) was dominant at the times of the previous cleanings.

**NH₄⁺-N oxidation efficiency**

Figure 6 shows the temporal change in NH₄⁺-N concentration. Despite the fact that the seeding bacteria were collected from a biofilter in which active nitrification occurred, almost no nitrification was observed in the early stage of the filter run. This might have been because of the very low water temperature (around 5°C). Nitrification increased as the water temperature rose. Even though almost complete nitrification was observed by the time when the first sponge cleaning was carried out, the nitrification efficiency declined considerably after the cleaning. This was probably due to the removal of the microorganisms fixed on the membrane. Three weeks were required for the nitrification efficiency to increase to a level similar to that observed just before the first cleaning. Stable nitrification was observed after that. However, the pressure difference rapidly increased in the same period and therefore the second sponge cleaning had to be conducted as described in the previous section.

After the second sponge cleaning, a part of the detached cake (corresponding to 4% of the whole cake) was returned to the membrane chamber in order to rapidly restore the nitrification efficiency. Dead-end filtration for fixation of the biomass was not carried out. These re-inoculation procedures were effective in increasing the nitrification efficiency in a laboratory experiment (Kimura et al., 2000). As can be seen in Figure 6, however, it took about one month to acquire good nitrification after the second cleaning. Stable nitrification had, however, been maintained since the middle of July even under the condition of high membrane flux (0.8 m/d). After the third cleaning, the same re-inoculation was carried out again. However, there was no rapid recovery of nitrification efficiency. The reason for this difference between the results of the laboratory experiment and those of the pilot study is not clear, and further study is needed to find an efficient method for biomass fixation after cleaning. It was thought that restoration of nitrification efficiency was difficult because the
water temperature had decreased below 10°C before nitrification became significant. In order to improve the nitrification efficiency, from December 10, 1999, phosphorus (K₂HPO₄) was directly added to the reactor to maintain the concentration of phosphorus in the feed water at 0.05 mg-P/L. This nutrient supplement significantly improved the nitrification efficiency. Nitrification efficiency was significantly improved one month after, even when the water temperature was less than 4°C.

Removal of other substances
In the pilot study, it was thought that various microorganisms other than nitrifiers were present in the biofilm that had developed on the membrane surface. Due to these microorganisms, it was thought that substances other than NH₄⁺-N were removed. Such substances as humic substances (UV absorbance at 260 nm, expressed as E₂₆₀), AOC, manganese, iron and aluminium were examined.

Humic substances expressed by E₂₆₀. Coagulation and sedimentation with the JMS resulted in removal of E₂₆₀, while the BMR did not reduce E₂₆₀ to any measurable extent (data not shown). Generally, coagulation is suitable for removal of high-molecular-weight organic substances but is not efficient for removal of low-molecular-weight organic substances. The effluent from the JMS can be expected to contain mainly low-molecular-weight organic substances that cannot be removed by the membrane employed (cut-off molecular weight: 750,000 Da). Adsorption of humic substances (often referred to as natural organic matter, NOM) by a biofilm has been investigated by Carlson and Silverstein (1998); however, this kind of “biosorption” of organic matter was not significant in this experiment.

AOC. Van der Kooij (1992) suggested that AOC concentrations should be less than 10 µg-C/L to limit the regrowth of heterotrophs during distribution. In this study, the AOC concentration was reduced to less than 10 µg-C/L, while AOC concentration in the raw water was more than 120 µg-C/L. Kasahara et al. (1998) carried out intensive AOC assessment at the same plant and concluded that it was difficult to reduce AOC concentration below 35 µg-C/L by using an advanced water purification system including coagulation, sedimentation, sand-filtration and biological activated carbon (BAC) with/without ozonation. These results indicate that the BMR is efficient in removing AOC and establishing biologically stable water.

Metals. Figure 7 shows the results of measurement of manganese concentration. On March 5, when the water temperature was still low and nitrification was not significant, there was little removal of manganese. With increase in water temperature (samples obtained on June
17, August 5 and September 18), manganese concentration decreased to low levels. This was probably due to biological oxidation of manganese. Rittmann and Snoeyink (1984) reviewed the close relationship between biological nitrification and biological manganese oxidation. The concentrations of iron and aluminium were both reduced to low levels regardless of water temperature (data not shown). The removal of iron and aluminium was, however, not due to microorganisms but due to the membrane sieve effect of iron and aluminium flocs.

Membrane fouling
As mentioned above, in the last part of the 17-month operation, sponge cleaning was less effective in reducing the membrane filtration resistance. This means that a large part of the filtration resistance was caused by irreversible membrane fouling. In order to obtain information on irreversible membrane fouling caused by organic substances, the fouled membrane was wiped with a sponge and then analyzed by Fourier transform infrared (FT-IR) microscopy. A comparison of the FT-IR spectrum of the fouled membrane with one of a new membrane showed that there was almost no significant increase in the IR peak (data not shown), indicating that irreversible accumulation of organic substance on the membrane was minimal. The fouled membrane that had been wiped with a sponge was also subjected to elemental analysis, which enabled detection of elements with element numbers greater than sodium. The results of this analysis showed that the major element on the fouled membrane was manganese (76% on a weight basis). At the end of the operation, the effect of sequential chemical membrane washing using hydrochloric acid (pH = 2.0), 0.1% oxalic acid and 0.1% sodium hypochloride was examined in this order. The results of the cleaning are shown in Figure 8. Cleanings using hydrochloric acid and oxalic acid were found to be effective enough in canceling the irreversible membrane fouling. These results suggest that manganese compounds mainly caused the irreversible membrane fouling in this pilot study.

Summary
The experimental results obtained from a pilot study in which the performance of a BMR was examined can be summarized as follows.
1. A pilot-scale filter run was successfully carried out. By implementation of pre-treatment (coagulation and sedimentation) and the sponge cleaning, the filter run could be continued for about 17 months without any chemical washing.
2. Sufficient nitrification was observed when the water temperature was high. Deterioration in the nitrification efficiency during winter could be reduced by the addition of phosphorus. However, further study is needed to find a method for rapid recovery of the nitrification efficiency after sponge cleaning.

![Figure 8](https://iwaponline.com/ws/article-pdf/2/2/177/408226/177.pdf)
3. In addition to nitrification, biological oxidation of AOC and manganese can be expected with the BMR. In this study, both AOC and manganese concentration in the permeate decreased to a level less than 10 µg/L.

4. Irreversible membrane fouling, which was thought to be caused by manganese, became significant as the operation period became longer.

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