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Membrane fouling control and contaminant removal during direct nanofiltration of surface water

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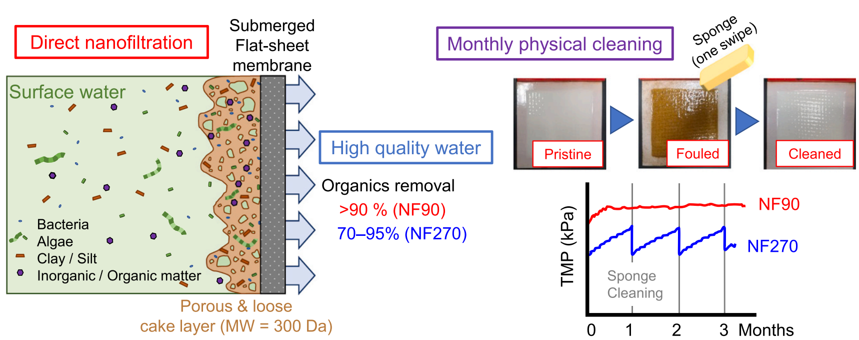
HIGHLIGHTS

- Direct nanofiltration (NF) of surface water was evaluated using submerged NF modules.
- Organic removal by the NF90 and NF270 membranes was >90 % and 70–90 %, respectively.
- Direct NF treatment at a low permeate flux of 2.5–5.0 L/m^{2}h formed a fluffy cake layer.
- Cake layer was mainly composed of organics with a molecular weight > 300 Da.
- One-wipe sponge cleaning removed all the foulants from the membrane surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Direct nanofiltration (NF) is an attractive separation process that produces high-quality drinking water without pretreatment. However, the propensity for membrane fouling is a considerable challenge. This study evaluated the potential of direct NF treatment of surface water using submerged flat-sheet (polyamide composite) NF membranes to achieve stable operation and high-quality water production. Direct NF treatment at a constant permeate flux of 5.0 L/m^{2}h (NF270) and 2.5 L/m^{2}h (NF90) was successfully continued for over 100 d with a monthly one-wipe sponge cleaning. Sponge cleaning eliminated the foulants on the NF270 membrane surface, thereby recovering the membrane permeability. Contrastingly, tight NF90 membranes did not exhibit significant changes in membrane permeability. The rejection of odorous compounds and other dissolved organic matter by the NF90 membrane was significant (>95 %), whereas those by the NF270 membrane considerably varied with the feed temperature. Further investigation suggested that the visible foulant on the membrane surface could be a porous cake layer mainly composed of constituents with a molecular weight of >300 Da, resulting in low hydraulic resistance. One-wipe sponge cleaning can readily detach fluffy cake layers. The results of this study suggest the viability of direct NF treatment as a low-energy advanced drinking water treatment system.

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1. Introduction

Water treatment using nanofiltration (NF) membranes is a powerful separation technology for producing clean water from contaminated sources such as groundwater, surface water, seawater, and wastewater [1–4]. The NF membranes have a pore size of 0.5–2 nm, corresponding to a molecular weight cut-off (MWCO) of 200–1000 Daltons (Da) [4]. Due to their small pore size, the ability of NF membranes to remove small organic compounds is better than that of commonly adopted coarser membranes, such as ultrafiltration and microfiltration membranes. NF membranes can remove low-molecular-weight constituents, including emerging organic micropollutants [5–7], fluoride from groundwater [8], and multivalent ions during desalination [9]. NF membranes can achieve higher organic removal than advanced water treatments, such as ozone and biologically activated carbon, which provide high-quality water [10,11]. However, severe fouling of NF membranes remains an ongoing challenge.

Generally, pretreatment is performed before the NF process to minimize membrane fouling. As spiral-wound NF membrane elements have narrow channels, the entry of the NF membrane element can be readily clogged by particles or organics in the feed without a pretreatment process [12–15]. Furthermore, membrane fouling on the membrane surface, particularly with dissolved organic matter [16], decreases permeate flux and increases energy consumption and chemical use. The pretreatment process allocated before the NF treatment can include ultrafiltration, microfiltration, rapid sand filtration, and ion exchange resins [6,17]. However, pretreatment requires high capital and operational costs; thus, the absence of a pretreatment process is advantageous for promoting the spread of NF membrane applications.

Direct NF treatment without a pretreatment process is an attractive alternative for improving the feasibility of NF treatment [18–22]. Two previous studies [23,24] have adopted submerged flat-sheet NF membrane modules to directly treat surface water and wastewater. The submerged flat-sheet NF membrane modules operate only at low transmembrane pressure (TMP) and permeate fluxes. Therefore, slow membrane fouling occurs while maintaining high membrane permeability. Two previous submerged NF membrane studies [23,25] have assessed the membrane fouling propensity of one specific commercial NF membrane, namely NF270, over several months of treatment of surface waters. Because the performance of other commercial NF membranes has not been explored for direct drinking water treatment, their potential for fouling propensity and treated water quality remains unclear.

The significant advantages of submerged flat-sheet membranes over spiral-wound membranes include physical cleaning (e.g., sponge cleaning) to eliminate foulants from the membrane surface instead of typical chemical cleaning [26–29]. Our previous study [24] assessed the impact of sponge cleaning after treating secondary wastewater effluent with an NF270 membrane, and it successfully eliminated the membrane foulants and recovered the membrane permeability. However, sponge cleaning was performed on only one cleaning occasion during wastewater treatment. The potential of direct NF treatment of surface water with multiple sponge cleaning occasions and the mechanisms of eliminating the foulants by sponge cleaning is yet to be revealed.

This study aimed to assess the validity of direct NF treatment of surface water using submerged flat-sheet NF membranes to achieve stable operation and high-quality drinking water as a sustainable advanced drinking water treatment process. The stability of their operation and the treated water quality using two polyamide composite NF membranes (NF90 and NF270) were assessed by tracking changes in TMP with monthly sponge cleaning. The treated water quality parameters included conductivity and dissolved organics, including odorous chemicals (geosmin and 2-methylisoborneol <2-MIB>).

2. Materials and methods

2.1. Submerged NF membranes

Commercial flat-sheet NF membranes NF90 and NF270 (DuPont/FilmTec) were used in this study. The NF90 membrane is a polyamide composite NF membrane with a pure water permeability of 10 L/m^2hbar. The NF270 membrane is a polypiperazine-amide composite NF membrane with a pure water permeability of 14 L/m^2hbar. Thin-film composite NF membranes were designed for organic matter and partial softening. According to the manufacturer's specifications, the removal of magnesium sulfate is >97.0 % at a $MgSO_4$ concentration of 2000 mg/L, TMP of 0.48 MPa, feed temperature of 25 °C, and recovery of 15 %. The MWCO of the NF90 and NF270 membranes are 200 and 300 Da, respectively. A submerged flat-sheet module was produced using an acrylonitrile butadiene styrene frame, a spacer, and two cut pieces of NF membranes. The submerged membrane modules were fabricated in an outside-in-flow orientation. Each module's effective membrane surface area was 242 cm^2 (each side had a width of 11 cm and a height of 11 cm).

2.2. NF filtration systems

The laboratory-scale submerged flat-sheet NF system consisted of a 0.9-L acryl membrane tank (3-6760-04, AS ONE, Osaka, Japan) with a water volume of 0.79 L. An overflow nozzle was installed to discharge the concentrate from membrane tanks. The membrane tank contained two membrane modules (i.e., NF270 and NF90). The permeate stream of each membrane module was connected to a pressure gauge and peristaltic pump (EYELA MP-4000; Tokyo Rikakikai, Tokyo, Japan) (Fig. 1). Concentrates and permeates were collected in 2-L beakers placed on a digital balance (EK-4100i, A&D Company; Tokyo, Japan).

A pressurized NF system (Supplementary Material, Fig. S1) was also used in this study. The crossflow NF system consisted of a 5-L stainless steel feed tank, high-pressure feed pump (20NHD15Z, Nikuni; Kawasaki, Japan), stainless-steel NF membrane cell (CF042, Sterlitech; Auburn, WA, USA), digital flow meters, two pressure gauges, a needle valve, and a temperature control unit coupled with a heat exchange coil (NCB-500, Tokyo Rikakikai; Tokyo, Japan). The effective membrane area of the cell was 42 cm^2.

2.3. Chemicals and feed water

Geosmin and 2-MIB solutions were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Potassium hydrogen phthalate was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Ultrapure water was prepared with a Simplicity® UV Water Purification System (Sigma-Aldrich, Tokyo, Japan). Dam water was collected six times from a water treatment plant in the Nagasaki Prefecture, Japan (Supplementary Material, Table S1).

2.4. Experimental protocols

The system was operated at constant permeate fluxes (J) of 2.5 and 5.0 L/m^2h for the NF90 and NF270 membranes, corresponding to a 1.0 and 2.0 mL/min flow rate, respectively. The dam water in the feed reservoir was pumped (Q-100VF-P-S; TACMINA, Osaka, Japan) into the membrane tank as the feed water to achieve an overall permeate recovery of 60–90 %. The TMP was measured in real time. Due to the occurrence of a slight discrepancy between the target (J_{target}) and recorded (i.e., actual) permeate fluxes (J_{actual}), TMP (kPa) was corrected using the following formula:

$$TMP_{corrected} = TMP_{actual} \times J_{target} / J_{recorded} \quad (1)$$

The temperature of the dam water in the feed reservoir and

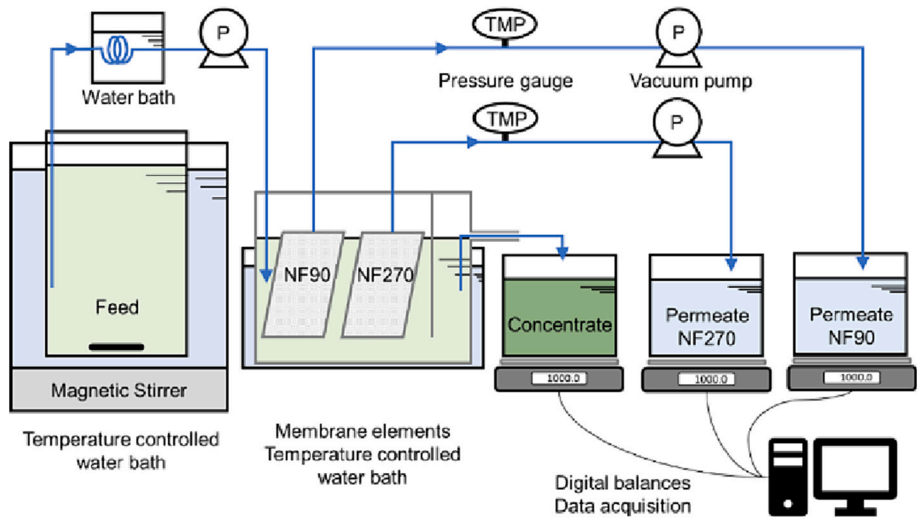

Fig. 1. Schematic diagram of laboratory-scale submerged system using flat-sheet NF membranes.

membrane tank were kept at 5 and 25 ± 0.5 °C, respectively. The two membrane modules were removed monthly from the membrane reservoir for cleaning. Each module underwent gentle one-wipe physical cleaning using a high-quality polyurethane sponge (AMS-363H; AS ONE, Osaka, Japan) to remove the fouling layer. The physical cleaning was performed with the sponge using horizontal strokes without applying pressure on the membrane surface, and each membrane surface was rinsed with approximately 10 mL of pure water. The cleaning uniformity was confirmed by taking photos before and after the cleaning. Water quality analyses were performed 2 h before and 2 h after one-wipe sponge cleaning to evaluate the impact of sponge cleaning. After 102 d, the NF270 membrane module was replaced with a new NF270 membrane module.

The pressurized NF treatment was performed with constant permeate fluxes of 25 and 50 L/m^{2}h for NF90 and NF270 membranes, respectively. This corresponded to flow rates of 1.75 mL/min (NF90) and 3.5 mL/min (NF270) at a feed temperature of 25 ± 0.5 °C for 8 h. The crossflow rate was maintained constant at 0.5 L/min during the filtration. The concentrate and permeate were recirculated into the feed reservoir.

2.5. Analysis

2.5.1. Water quality analysis

Water quality analyses included conductivity, pH, $E_{254,}$ and dissolved organic carbon (DOC) concentration. The conductivity was measured using a conductivity meter (LAQUA twin EC-33B, Horiba, Kyoto, Japan). The pH was measured using a pH meter (MM-41DP; TOADKK, Tokyo, Japan). The UV absorbance E_{254} was measured at 254 nm using a spectrophotometer (UV-1280, Shimadzu; Kyoto, Japan). Turbidity was determined using a turbidity meter (2100Q; Hach, Loveland, CO, USA). DOC concentrations were determined using a TOC-L analyzer (Shimadzu, Kyoto, Japan) calibrated with 0, 2.5, 5, and 10 mg/L potassium hydrogen phthalate. The feed and concentrate samples were filtered using a 0.45-μm pore size filter before E_{254} and DOC analysis (USEPA Method 415.3). To assess the removal of organic matter and ions, the rejection of DOC, E_{254}, and the conductivity were calculated as follows:

$$\text{Rejection } (\%) = 100 \times \left(C_{f-c} - C_p\right) / C_{f-c} \quad (2)$$

where $C_{f\text{-}c}$ is the average feed and concentrate concentration, and C_p is the permeate concentration.

2.5.2. Organic matter analysis

The organics in the feed, concentrate, permeate, and fouling layers were characterized by analyzing their excitation-emission matrix (EEM) fluorescence spectra using an RF-6000 spectrophotometer (Shimadzu; Kyoto, Japan). The fouling layers were collected with a sponge during physical cleaning of the membranes and resuspended in ultrapure water. The DOC concentrations of the fouling layers were adjusted to 2 mg/L before the EEM analysis. The spectra were corrected by subtracting the spectrum of ultrapure water. The dam water was analyzed using an LC-OCD system (DOC-LABOR, Karlsruhe, Germany) to identify dissolved organic matter. The mobile phase used in the system was a phosphate buffer containing 2.5 g/L KH_2PO_4 and 1.2 g/L $Na_2HPO_{4.}$ Details of the LC-OCD analysis can be found in an earlier study [30].

2.5.3. Odorous compound concentrations

On the 75th day, odorous compound rejection by the NF membranes was tested. A stock solution of geosmin and 2-MIB was added to 5 L of feedwater at a 200 ng/L concentration. The feed temperature was changed to 13, 25, and 35 °C to assess the effect of seasonally variable temperature on geosmin and 2-MIB rejection. After system stabilization for >120 min, permeate, feed, and concentrate samples were collected. The concentrations of the odorous compounds in the samples were determined via gas chromatography–mass spectrometry (GC-2030 (GC), QP2020NX (MS), Shimadzu, Kyoto, Japan) using the purge and trap method (PT7000), AS7100-238, GL Sciences, Tokyo, Japan). After the odor rejection test, the feed water containing the odorous compounds was discharged and replaced by the dam water.

2.5.4. Membrane characterization

At the end of the filtration tests, the fouled membranes were removed from the tank to evaluate the surface of the fouled and cleaned membranes. The NF membranes were cut into squares of approximately 5 cm. Some membrane pieces were cleaned with a sponge to replicate physical cleaning. The cleaned and fouled membranes were stained with 1 μL of Live/Dead™ Baclight™ Bacterial Viability kit (Thermo Fisher Scientific; Tokyo, Japan) dissolved in 50 μL of ultrapure water. Excess liquid was removed after 15 min of incubation in the dark, and the membranes were observed under a fluorescence microscope (BZ-X800; Keyence Co., Osaka, Japan). The contact angles of the clean and fouled NF membranes were measured using an automatic contact angle meter (SImage AUTO 100; Excimer, Kanagawa, Japan) and Milli-Q water.

3. Results and discussion

3.1. Membrane fouling and cleaning

3.1.1. Changes in TMP

Direct NF treatment of the dam water resulted in the gradual accumulation of foulants on the membrane surface over 100 d. In the case of NF90, membrane fouling occurred during testing. The TMP of the NF90 membrane increased from 50 to 60 kPa during the first 3 d, and thereafter, it remained stable between 60 and 70 kPa until the end of the study (Fig. 2). It is noted that the fluctuations in the feed flow rate occurred after 95 d without changes in the feed pump settings. The reduced feed flow rates resulted in a high-water recovery of >70 %. However, the high-water recovery of 70–90 % did not cause a visible impact on the TMP trend. Sponge cleaning on days 30, 60, and 91 did not affect TMP recovery. However, visible foulants were entirely removed by sponge cleaning (Fig. 3). These results imply that the membrane foulant deposited on the membrane surface did not contribute to hydraulic resistance after the initial membrane fouling development. The retention time of the feed in the membrane tank was approximately 4 h, and bacteria on the membrane surface may have played a role in the negligible increase in TMP. The level of their contribution to suppressing the increase in the TMP was beyond the scope of this study, and this pending question will be comprehensively addressed in future studies.

The NF270 membrane underwent progressive membrane fouling. TMP increased from 48 to 67 kPa until day 30 (Fig. 2). Sponge cleaning on day 30 decreased the TMP from 68 to 45 kPa. The results resemble an earlier study on wastewater (Ngo et al., 2021), demonstrating permeability restoration by sponge cleaning. Similarly, during the second and third filtration cycles, the TMP gradually increased to 59 kPa and 61 kPa until days 60 and 91, respectively. Sponge cleaning commonly reduced the TMP to 44–45 kPa and entirely removed foulants from the membrane surface (Fig. 3). The TMP of the cleaned NF270 membrane was equivalent to that of the new NF270 membrane module at 102 d (44 kPa). The results indicate that the foulants on the NF270 membrane can cause hydraulic resistance, although they can be entirely removed by sponge cleaning.

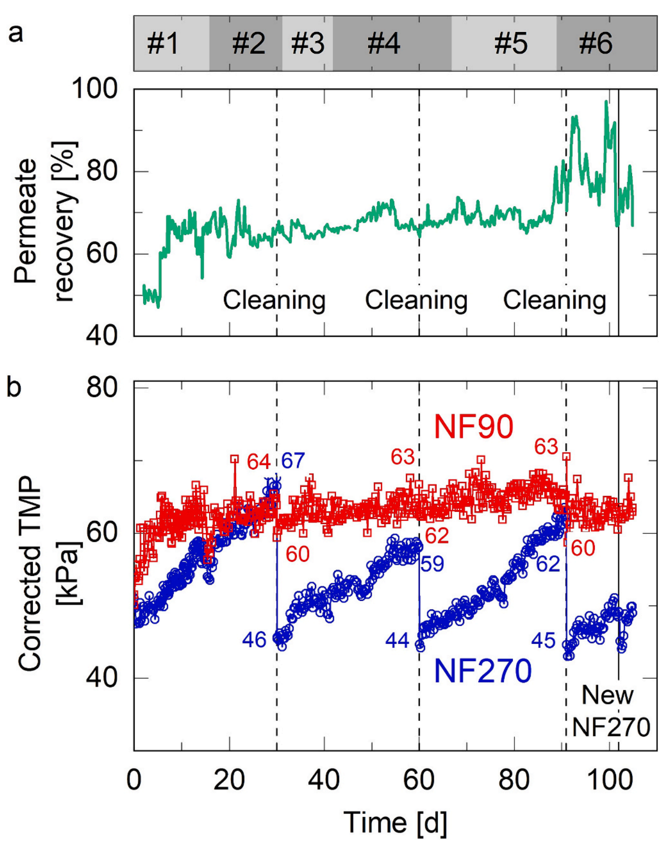

Fig. 2. Plots depicting (a) permeate recovery and (b) corrected TMP during NF treatment of the dam water by NF270 and NF90 membranes (constant permeate flux of 2.5 L/m^{2}h (NF90) and 5.0 L/m^{2}h (NF270) and feed temperature of 25 °C). The values indicate TMP recorded 2 h before and 2 h after cleaning on days 30, 60, and 91. The number on the top indicates the dam water collected during different sampling occasions.

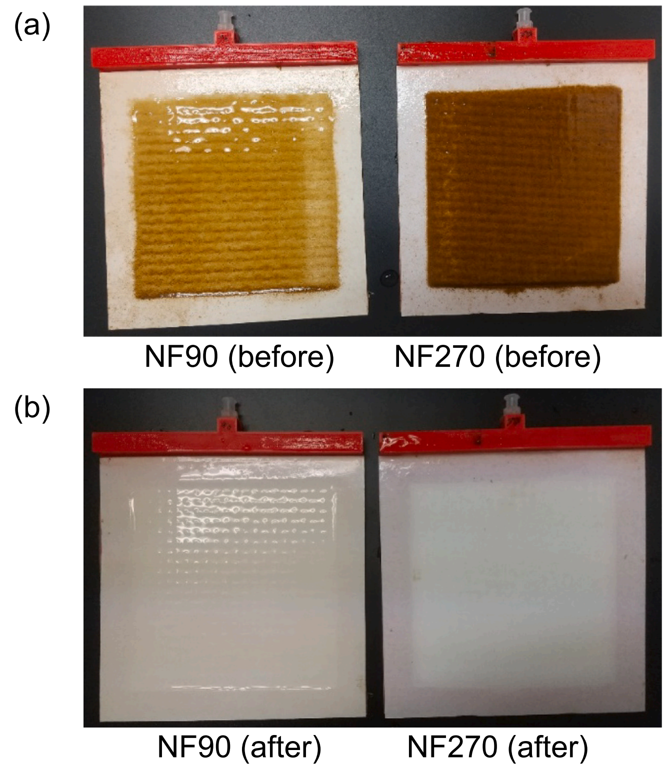

Fig. 3. Photographs of the NF90 and NF270 membrane surface (a) before and (b) after the first sponge cleaning on day 30. Feed water #1 and #2 were used until the first cleaning on day 30. The other cleaning photos attained on days 60 and 91 are shown in Supplementary Material, Figs. S2 and S3.

3.1.2. Characterization of membrane foulants

At the end of the tests (105 d for NF90 and 102 d for NF270), the membranes obtained from the membrane tank were disassembled and analyzed for membrane and foulant characterization. Organic foulants on membrane surfaces generally alter their physicochemical properties and increase their surface hydrophobicity [31,32]. Similarly, the contact angle analysis in this study showed an increase in contact angle from intact to fouled membranes, indicating that the membrane became hydrophobic with the membrane foulant (Fig. 4). However, sponge cleaning reduced the contact angle to a near-original value. The results indicate that sponge cleaning eliminated the foulants on the membrane surface.

To characterize the organic foulants, the feed water and fouling layers removed from the membrane surface by sponge cleaning were analyzed using spectrophotometry. The feedwater EEM spectra showed five peaks (Fig. 5a and b). Peaks A [Ex/Em = 237–260/400–500 nm], C [Ex/Em = 300–370/400–500 nm], and M [Ex/Em = 312/380–420 nm] represented humic-like substances, with peak M indicating microbial humic-like substances [33]. Peaks T_1 [Ex/Em = 270–280/320–350 nm] and T_2 [Ex/Em = 215–237/340–381 nm] correspond to tryptophan-like substances (protein-like substances) and have a relatively high fouling propensity [33]. The fluorescence peaks observed in this study are

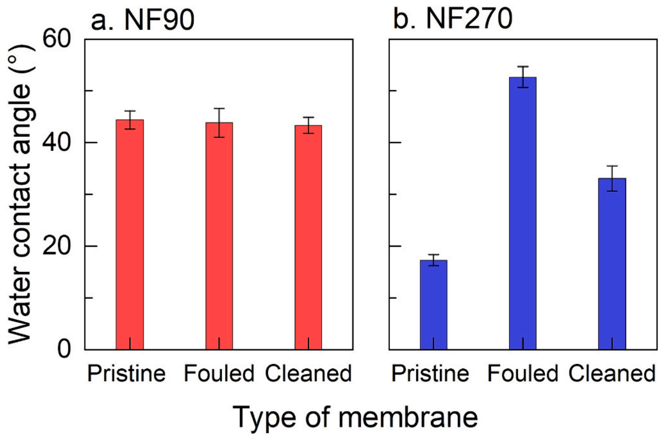

Fig. 4. Contact angle of pristine (new), fouled, and cleaned NF90 and NF270 membranes (average and ranges of six locations).

typical of dam water, where protein-like substances are dominant [34,35]. The foulants removed from the NF270 and NF90 membranes exhibited similar EEM fluorescence peaks at T_1 and T_2 (Fig. 5c and d). The results indicated that among fluorescent organic foulants, protein-like substances dominated, and humics were not major organic foulants in this study. The EEM spectra of the concentrate showed the highest intensities of the C and M peaks (Supplementary Material, Fig. S4). These results suggest that sponge cleaning can readily remove the foulants.

Biofouling is also a significant fouling phenomenon in long-term NF treatment [17]. The fouled membranes were observed by microscopy. Algae, including diatoms, green algae, and cyanobacteria, were found in the fouling layers (Supplementary Material, Fig. S6). After staining, the fouled and sponge-cleaned membranes were analyzed using fluorescence microscopy. Undamaged (alive) bacterial cells appear green in the images, whereas damaged (dead) bacterial cells are red. Most of the cells, including algae and bacteria, on the NF90 and NF270 membranes were undamaged (Fig. 6a). Although damaged bacterial cells are typically present in surface waters [36], undamaged bacterial cells were dominant on the membrane surface. This indicates the growth of bacteria attached to the membrane surface. Regardless of the difference in undamaged and damaged bacterial concentrations on the membrane surface, sponge cleaning eliminated almost all bacterial cells from the surface of both NF membranes (Fig. 6b). Overall, the results indicate that periodic physical cleaning can remove nearly all the bacteria on the membrane surface.

3.2. *Water quality*

3.2.1. *General water quality parameters*

The ability of the direct NF treatment to produce high-quality water was assessed during the test period. During dam water sampling, the feed water quality varied. For example, the turbidity in the feed water varied from 2.8 to 18.7 NTU (Supplementary Material, Fig. S7). Similarly, DOC concentrations, UV absorbance E_{254} (an indicator of humic acid concentrations), and conductivity in the feed varied at 1.3–2.4 mg/L, 0.03–0.05 Abs, and 113–150 μS/cm, respectively (Supplementary Material, Fig. S8). The quality of the NF90 permeate remained low throughout the study at an E_{254} of <0.0025 Abs, a DOC concentration of <0.25 mg/L, and a conductivity of <38 μS/cm. As a result, the calculated removal of DOC and E_{254} by the NF90 membrane was high at >90

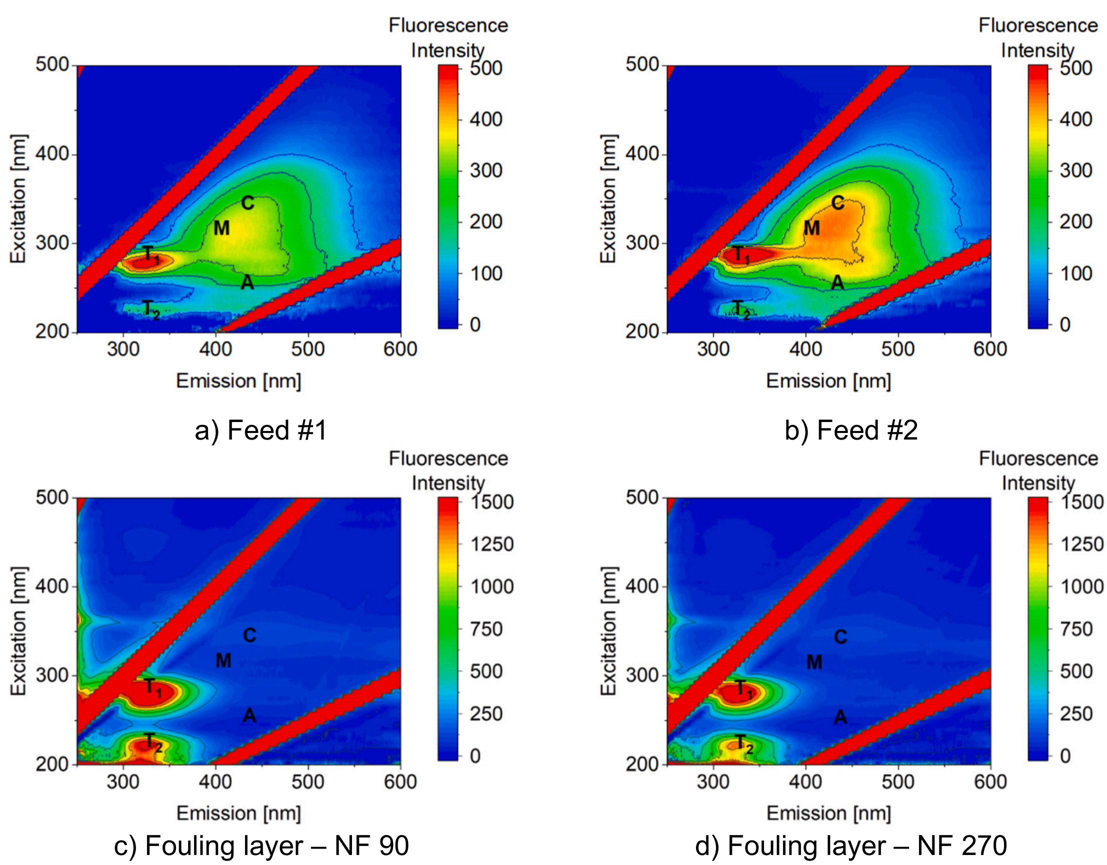

Fig. 5. Gradient plots illustrating the excitation-emission matrix fluorescence spectra of the (a) feed water #1 and (b) feed water #2, and the foulants extracted by the sponge cleaning from the fouled (c) NF90 and (d) NF270 membranes on day 30. The DOC concentrations of the fouling layers were adjusted to 2 mg/L before EEM analysis. The foulants extracted by the sponge cleaning from the fouled membranes on days 60 and 91 are available in Supplementary Material, Fig. S5.

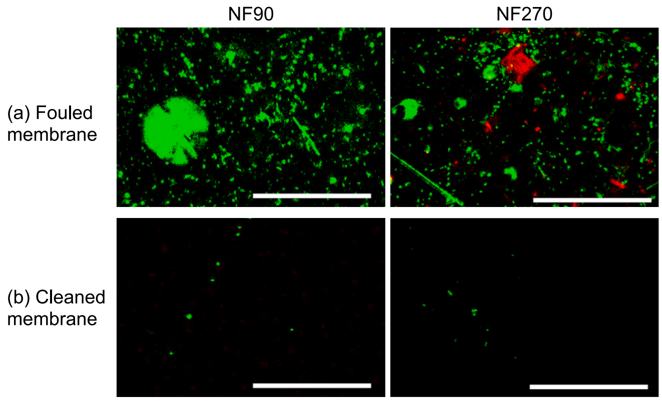

Fig. 6. Microscopic fluorescence images of (a) the fouled and (b) sponge-cleaned NF membranes. The live/undamaged cells appear in green, and the dead/damaged cells appear in red in the images. The white bar represents 50 μm.

% (Fig. 7). The removal of conductivity was low but sufficiently high at 72–85 %.

The water quality of the NF90 permeate was generally superior to that of the NF270 membrane. Low removal of conductivity (i.e., ion concentration) of 23–46 % is typical for NF membranes because they mainly remove multivalent ions [37]. The low conductivity removal can be explained by the smaller pore size of the membrane NF90 than that of NF270 [38,39]. High-conductivity removal is not necessary to comply with water regulations unless the surface water is saline. The rejections of absorbance E_{254} and DOC by the NF270 membrane were found at 75–97 % and 67–95 %, respectively (Fig. 7). Particularly, from days 50 to 84, the rejection of E_{254} and DOC decreased to 75 and 72 %, respectively. Although E_{254} and DOC rejection recovered slightly after physical cleaning conducted on day 91, the rejection of DOC and E_{254} continued to decrease until day 102, when the initial NF270 module was replaced with a new NF270 module.

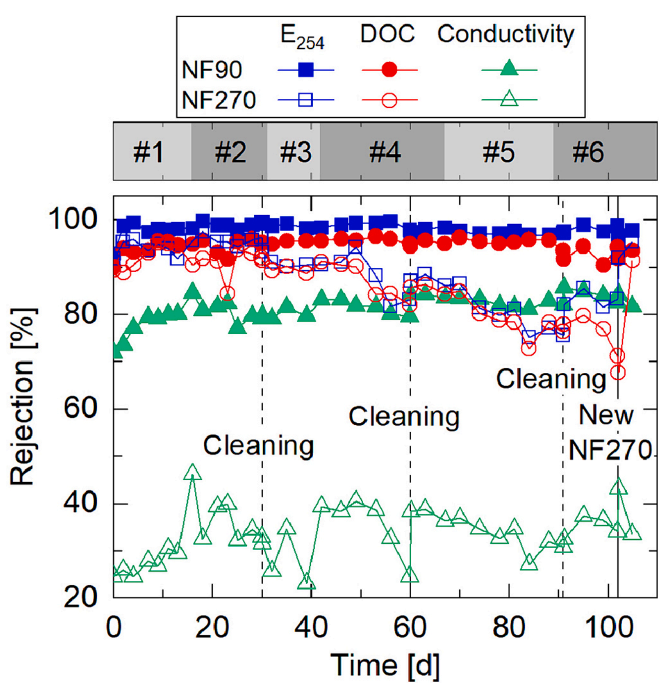

Fig. 7. Plot showing the rejection of E_{254}, dissolved organic carbon (DOC), and electrical conductivity during NF treatment of the dam water by NF270 and NF90 membranes (constant permeate flux of 2.5 L/m^{2}h (NF90) and 5.0 L/m^{2}h (NF270) and feed temperature of 25 °C). The number on the top indicates the dam water collected during different sampling occasions. The NF270 membrane module was replaced at 102 d.

On day 102, the NF270 membrane module was replaced with a new module. Subsequently, the rejection of all water quality parameters by the new NF270 membrane module was comparable to that at the beginning of the study. There are three potential reasons for this deterioration: membrane aging [40], integrity failure, or aging of the membrane frame. Commercial spiral-wound NF270 membranes can be used for several years. However, sponge cleaning may accelerate aging. As the conductivity removal by the NF270 membrane module did not deteriorate, it may have caused a reduction in the rejection of organics only. The integrity or aging of the membrane frame is another potential reason for this phenomenon. The frame was self-made using a 3D printer, and the reliability of the frame (or the adhesive to fix the membranes) was not as high as that of the commercial membrane module. Furthermore, the NF90 membrane module did not exhibit any variation in the removal ability over the test period. Although the number of modules tested at the laboratory scale was limited, the results indicated that validating the reliability of direct NF treatment is likely to require (i) >3 months of testing and (ii) multiple modules in parallel.

3.2.2. Odor compound rejection

On day 75, the rejection of odorous compounds (2-MIB and geosmin) by the two NF membrane modules was evaluated at three different feed temperatures after adding their stock solutions to the feed water. These two compounds are mainly produced by algae in surface waters and provide an unpleasant taste to drinking water. The dam water did not have 2-MIB and geosmin concentrations above the analytical detection limit. Generally, the NF90 membrane showed a high removal of odorous compounds. Regardless of the varied feed temperature from 13 to 35 °C, the membrane NF90 showed high geosmin and 2-MIB removal of 98.5–99.8 % and 98.4–94.0 % (Fig. 8). The high rejection of geosmin and 2-MIB by the NF90 membrane was consistent with the results of other studies [41,42].

Contrastingly, the removal of odorous compounds by the membrane NF270 was relatively low and varied considerably. The geosmin removal decreased from 77 % to 37 % when the feed temperature increased from 13 to 35 °C. Similarly, 2-MIB removal decreased from 47 % to 35 % for the same feed temperature changes. The rejection of 2-MIB

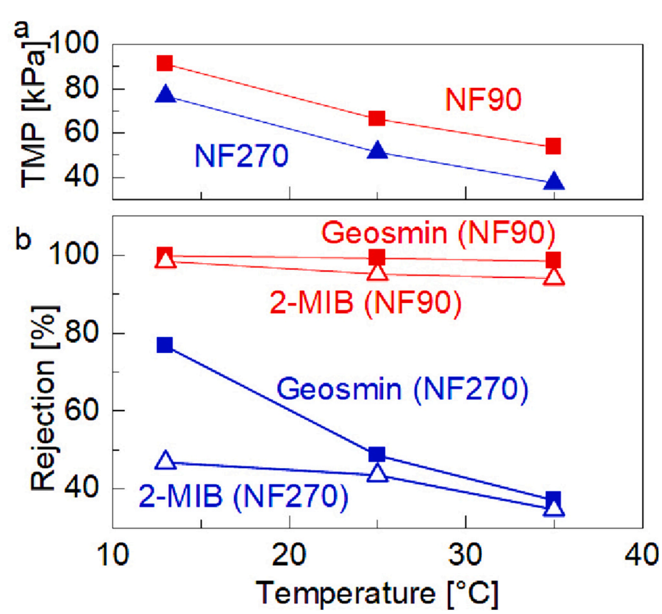

Fig. 8. Line graphs depicting (a) the corrected TMP and (b) the rejection of odorous compounds (geosmin and 2-MIB) during direct nanofiltration of the dam water by NF270 and NF90 submerged membrane modules at 13, 25, and 35 °C. The tests were conducted on day 75.

and geosmin by NF270 in this study was lower than that in the literature [43], with a removal of 68–85 % and 70–90 % for geosmin and 2-MIB, respectively. This is likely attributed to the low permeate flux (5.0 L/m^2h) due to the submerged orientation in this study. As the solute transport across the membrane changes slightly for various permeate fluxes, a high permeate flux can dilute the solute in the permeate, leading to high solute rejection [44,45]. The required rejection of these odorous compounds varies depending on their concentrations in the source water and local water quality regulations. The results indicate that the NF90 membrane can remove large amounts of odorous compounds, regardless of the submerged orientation and variable feed-water temperature. Contrastingly, the benefit of using submerged NF270 membrane modules for advanced drinking water treatment may be limited to meeting water quality regulations in specific climates (high-temperature water sources) and regions (stringent regulations).

3.3. Presumed mechanisms of membrane fouling control

The results of this study support the validity of a direct NF treatment without chemical cleaning. Direct membrane treatment generally requires frequent physical (e.g., backwashing) and chemical cleaning (soaking in a caustic solution); thus, the findings of this study are unique. To identify the cause of this unique observation, the mechanisms underlying the membrane fouling and sponge cleaning were determined. The cause of the slow progress of membrane fouling was first evaluated by comparing it with the fouling trend obtained using a pressurized cross-flow NF system at 10 times higher permeate fluxes of 25 and 50 L/m^2h for NF90 and NF270, respectively. The TMP of the NF90 membrane in the pressurized system increased considerably from 291 to 369 kPa in 8 h. Similarly, the TMP of the NF270 membrane increased from 224 to 397 kPa after 8 h. The results obtained under different permeate flux conditions were compared with the cumulative volume of the treated water rather than time (Fig. 9). The increase in the TMP in the submerged orientation was negligible for both NF270 and NF90 membranes, indicating that foulants deposited at a low permeate flux can induce less hydraulic resistance. These results imply that the applied lower permeate flux of the NF90 membrane (2.5 L/m^2h) can cause lesser membrane fouling and hydraulic resistance than that of the NF270 membrane (5.0 L/m^2h). A high TMP can cause compaction of the foulant layer, thereby increasing the hydraulic resistance [46]. Although a lower permeate flux requires a higher membrane surface area to produce a specific water volume, direct NF treatment in the submerged orientation is advantageous for avoiding frequent cleaning.

In addition to the difference in applied permeate flux, the different membrane fouling trends can be attributed to the difference in membrane tightness and properties. However, the difference in the membrane tightness (pore sizes) is unlikely to substantially impact the fouling trend because pore-clogging can be negligible based on membrane permeability recovery after eliminating membrane foulants from the membrane surface only. Although their membrane properties (polyamide for NF90 membrane and polypiperazine, similar to polyamide in chemical structure, for NF270 membrane) may have caused the difference in their membrane fouling trends, understanding the impact of membrane surface chemistry will require additional work under the same applied permeate flux and more controlled fouling conditions (e.g., use of model foulants), which will be explored in a future study.

The structure of the fouling layer was determined from the test results. Generally, the primary fouling mechanism of NF membranes is cake layer formation on the membrane surface [47,48]. The small sizes of the two NF membrane pores (MWCO <300 Da [44]) prevent large particles and high molecular weight (MW) molecules from entering the membrane pores. To clarify this, we characterized the size distribution of the dissolved organic constituents in dam water samples (Dams #2 and #4) using an LC-OCD chromatogram ((Supplementary Material, Fig. S9). Dissolved organic compounds were classified into four fractions: biopolymers, humic acids, building blocks, and low-molecular-

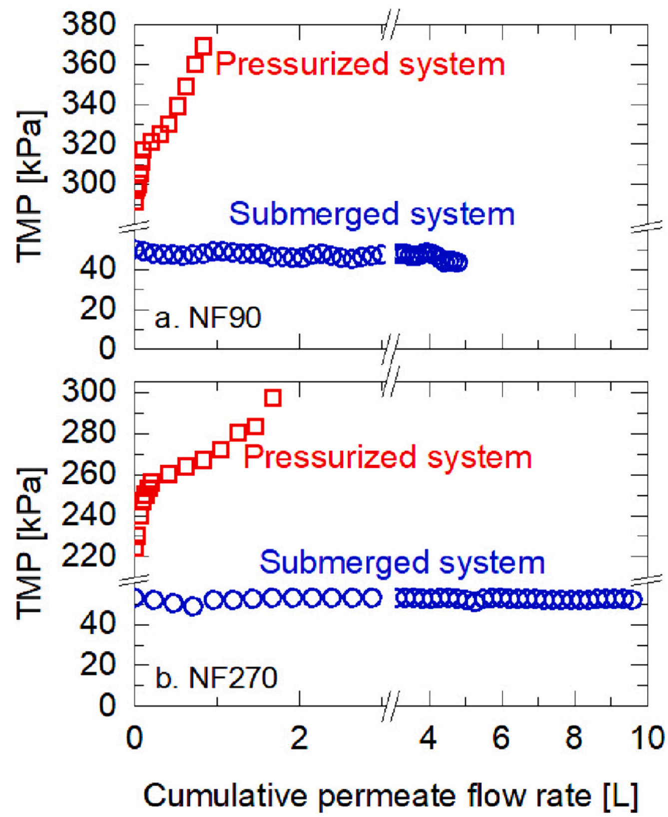

Fig. 9. Scatter plot showing the corrected TMP during NF treatment of the dam water by (a) NF90 and (b) NF270 membranes for submerged and pressurized systems. The permeate flux of the submerged NF system was 2.5 L/m^2h and 5.0 L/m^2h for the NF90 and NF270 membranes, respectively. The permeate flux of the pressurized NF system was 25 L/m^2h and 50 L/m^2h for the NF90 and NF270 membranes, respectively.

weight compounds (LMW). The dam water sampled on both occasions had a similar composition. The humic acids with an MW of approximately 1000 Da were the significant fraction of organics (51–61 %), and biopolymers (MW = ≥20,000 Da) were 15–20 % in fraction (Supplementary Material, Table S2). Building blocks (i.e., products of degradation of humic acids) (MW = 300–500 Da) represented <2.4 % of organics. LMW organics (MW ≤350 Da) represented 15–20 % of the fraction, and these small organics could pass through the NF270 and NF90 membranes. However, most organics in the dam water samples were hydrophilic (>86 %) and were less likely to be absorbed by the inner pore walls. LMW organics, such as protein-like organics and humics, were detected in the NF permeate (Supplementary Material, Fig. S4). Peak T_1 represents tryptophan-like substances (i.e., protein-like substances), such as tryptophan (204 g/mol), which can pass through NF membranes (MWCO = 200–400 g/mol) [49] and can be foulants in the inner pore walls of reverse osmosis membranes [50,51]. Therefore, it can be presumed that the organics passing through the membranes did not contribute to the hydraulic resistance.

Overall, particles (including algae and cells) and organics with MW >500 Da in the dam water were the main components of the cake layer on the membrane surface. Although LMW substances can permeate through NF membranes, some can be adsorbed onto the inner pore walls of the NF membranes and cause irreversible during the initial filtration stage; their contribution to the hydraulic resistance can be minor. The cake layer on the membrane surface may have progressively developed, and a dense cake layer, as shown in Fig. 3a, may have formed. However, the cake layer was porous and fluffily (not compacted) because of the low TMP applied in the submerged orientation (Fig. 10a). As a result, one-wipe sponge cleaning could remove all the fluffy cake layers from the membrane surface (Fig. 10b), resulting in a high recovery of membrane permeability. The same approach (i.e., direct surface-water treatment using submerged NF membrane modules and sponge cleaning) can be adopted for many tight NF membranes. Further assessments using different NF membrane types can help explain the presumed mechanisms.

3.4. Practical implications

The NF membranes used in this study underwent monthly one-wipe sponge cleaning. The frequency of sponge cleaning can vary depending on the operating conditions (e.g., permeate flux) and concentration and properties of foulant in water sources. Repeated cleanings can influence the lifetime and integrity of the NF membranes because the polyamide composite NF membranes are not designed for physical cleaning. During pure water treatment, an accelerated test was conducted to identify potential damages by wiping both sides of an NF270 membrane module 35 times (5 wiping/time × 7 times) (Fig. 11). As a result, the NF membrane permeability and separation performance did not change. However, because frequent cleaning with actual foulants (particularly with sharp inorganic substances) on the membrane surface can cause scratches in the long term, a countermeasure to protect the membrane surface from scratching damages during cleaning can be needed. For example, a membrane modification technique can provide a robust surface (e.g., grafting and coating). Existing coating techniques include polyvinyl chloride (PVC) and graphene oxide (GO).

Other essential factors include selecting the NF membrane type and the preset permeate flux before scaling up the submerged NF process. This study found that membrane fouling on the looser NF270 membrane progressed rapidly, considering its two-fold higher permeate flux than the tighter NF90 membrane. Fast membrane fouling requires frequent

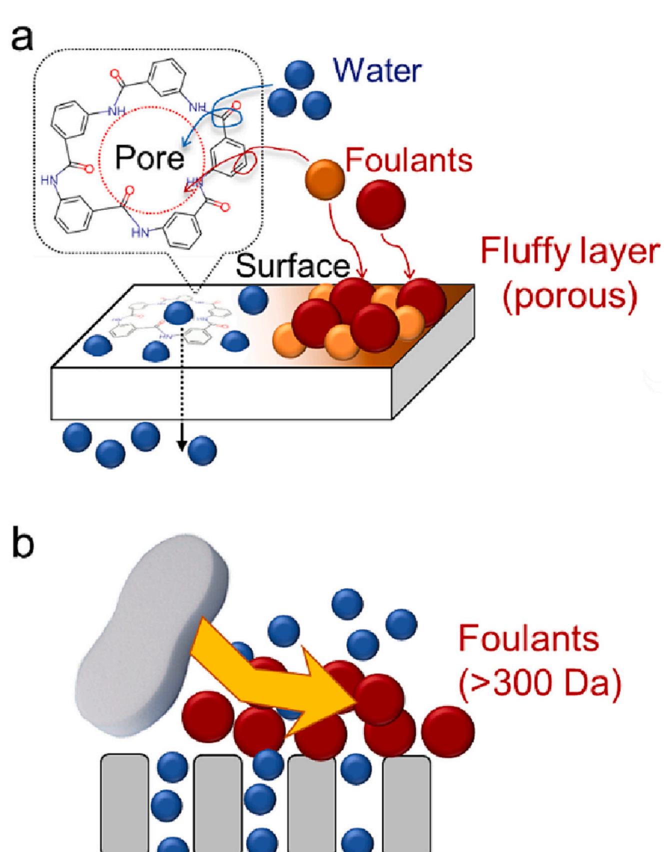

Fig. 10. Graphical illustration of a) fouling on the flat-sheet NF membrane surface under low permeate flux and b) removing foulant with a sponge.

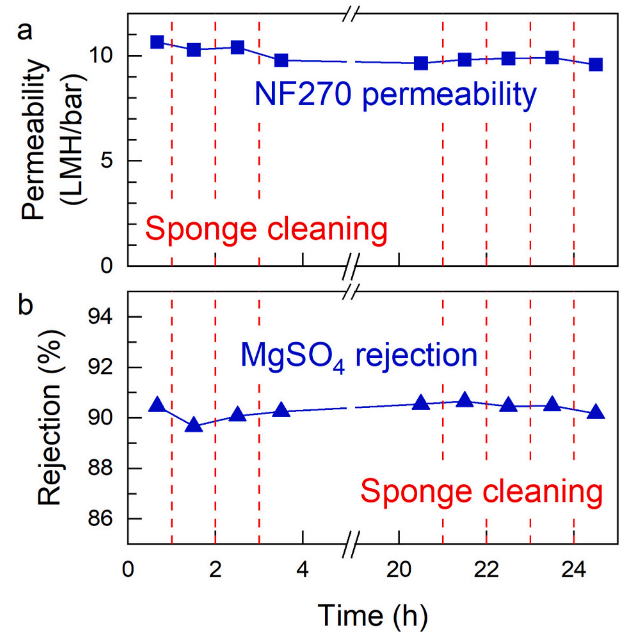

Fig. 11. a) The permeability of NF270 membrane and b) the rejection of $MgSO_4$ over time. The test was effectuated at a TMP of 42 kPa, feed temperature of 20 °C, and a feed $MgSO_4$ concentration of 5 mM. During the accelerated test, the membrane surface was wiped with the sponge five times, simulating five-time cleanings, and it was repeated seven times (total sponge cleaning = 35 times).

sponge cleaning, which can result in frequent membrane replacement. However, a lower permeate flux requires a larger membrane surface area, which increases the cost. Within the limitation of the TMP in the submerged orientation (approximately 100 kPa), the critical permeate flux that can achieve the minimum TMP increase should be explored in future studies. Furthermore, membrane selection considerably affects permeate water quality; a tighter NF membrane can provide higher water quality. As a result, decisions on membrane-type selection (i.e., manufacturing and model number) must be made based on a fit-on-purpose approach. Further, an economic analysis of direct nanofiltration using submerged NF membranes in comparison with other advanced drinking water treatment processes is needed for future studies.

4. Conclusions

Direct NF of dam water in submerged NF90 and NF270 membrane modules at a low permeate flux resulted in a slow increase in the TMP. A monthly physical cleaning with a sponge removes all the significant foulants, including bacteria, from the membrane surface. The fouling trends can vary depending on the NF membrane selection. High-quality water with >90 % removal of organics, including odorous compounds (geosmin and 2-MIB), was provided by a tight NF90 membrane. Otherwise, the NF270 membrane initially provided >90 % organic removal, gradually decreasing from 95 % to approximately 70 %. The removal of odorous compounds by the NF270 membrane varied considerably depending on changes in feedwater temperature. With a low permeate flux and TMP during direct NF treatment, this study identified that a porous and fluffy cake layer, including protein-like substances >300 Da, was the major contributor to hydraulic resistance. Furthermore, a one-wipe sponge cleaning can readily remove the fouling layer. The results of this study demonstrate that direct NF treatment of surface water coupled with sponge cleaning can provide stable operation and high-quality water over an extended period. The results of this study support the viability of direct NF treatment as a low-energy advanced drinking water treatment system.

CRediT authorship contribution statement

Sandrine Boivin: Writing – original draft, Validation, Investigation, Formal analysis. **Takahiro Fujioka:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2024.117607.

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