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Water impact statement

This study revealed that repeated pressurization caused integrity loss at the surface of reverse osmosis (RO) membrane resulting in a dramatic decrease in virus removal. This result highlighted the unique susceptibility of RO membranes for household water treatment and provided a key possible indicator (i.e. total pressurized times) determining the frequency of membrane replacement.

Impact of repeated pressurization on virus removal by reverse osmosis membrane for household water treatment

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Abstract

The reverse osmosis (RO) membranes are commoditized and available as household water treatment (HWT) in the areas where the access to safe water is limited. The RO membranes for HWT (residential RO) are typically operated intermittently without a cleaning process. This suggests a unique mechanism of membrane deterioration, as membrane oxidation, one of the main cause of RO membrane deterioration in industrial settings (desalination, wastewater reclamation), is not involved. Furthermore, the intermittent operation loads repeated shear stress on membrane surface. This study aimed to evaluate the impact of repeated pressurization on virus (bacteriophage MS2 and φX-174) removal by residential RO and to determine the location of integrity loss. We repeatedly pressurized and de-pressurized spiral-wound residential RO membranes for up to 10,000 cycles, while periodically evaluating virus removal. *E. coli* removal was also determined after 10,000 cycles. Moreover, these membranes were examined for virus and *E. coli* removal in flat-sheet configuration. For the first 3,000–4,000 cycles, φX-174 removal was maintained at approximately 4 log10 (99.99%), and then dramatically decreased. After 10,000 cycles, even *E. coli* leaked from the membrane. The deterioration of virus removal in flat-sheet configuration indicates integrity loss at membrane surface. Therefore, repeated pressurization deteriorated the virus removal performance of residential RO. The number of times that the RO membrane can be pressurized should be included as a criterion to determine the frequency of membrane replacement in residential RO.

1. Introduction

Reverse osmosis (RO) membrane is used for desalination and wastewater reclamation[1,2] because of its high efficiency for the removal of organic and inorganic contaminants,[3,4] as well as pathogens.[5] Owing to cost reduction and price competition,[6] the RO membrane was commoditized and made available even in households as point-of-use (POU) devices.[7,8] In developed countries, POU devices with RO membrane (RO-POU) have been installed in remote areas where the residents use private wells that are possibly contaminated with heavy metal or affected by high salinity of the water.[9] Currently, the market for RO-POU devices is rapidly growing in developing countries where access to safe drinking water is limited.[10,11] For example, previous studies have revealed that 31 – 43 % of households in urbanized areas of Hanoi, Vietnam use RO-POU.[12–14] This is likely attributable to the increased purchasing capacity of local residents and growing concern about the quality of drinking water. Furthermore, RO-POU may be used more widely considering that household water treatment (HWT) gains more interests because of the Sustainable Development Goals 6.1, achieve universal and equitable access to safe and affordable drinking water for all. World Health Organization (WHO) regards HWT as a proven intervention to improve drinking water quality and expects it to assist in achieving the goal.[15] Hence, some countries, such as Tanzania and Ethiopia, includes targets of scale-up HWT as national policies.[16] RO-POU is one of the possible options of such HWT given the high removal performance of RO membrane.

RO membrane for household water treatment (residential RO) has unique characteristics compared to that used for desalination or wastewater reclamation (industrial RO) (Table 1). Firstly, residential RO membrane has a smaller surface area, greater permeability, and lower salt removal capacity than industrial RO. Secondly, residential RO membrane is operated without any maintenance, while industrial RO membranes are periodically cleaned with chemical agents, such as low or high pH solution and non-oxidizing biocides (e.g., 2,2-Dibromo-3-nitrilopropionamide (DBNPA)), to mitigate fouling problems.[17] Finally, the operation of a residential RO membrane is typically intermittent; the membrane is pressurized every time the RO treated water is used, while that of industrial RO membrane is constant and continuous.

The high removal efficiency of RO membrane suggests that the permeate of RO-POU contains a low level of salts and microbes. According to a study on the rejection of electrical conductivity (EC).[18] more than half of the RO-POU devices in households removed > 90 %, while 5% of the devices removed < 40%. Another study focused on the occurrence of bacteria in the permeate of RO-POU where coliforms were detected from

the 40% of tested households.[19] These results suggest the deterioration of the residential RO membrane. Therefore, it is necessary to elucidate the mechanism of membrane deterioration so that membranes may be properly maintained.

The mechanism of membrane deterioration can be classified based on the location of integrity loss: membrane surface (pinhole, abnormally large pores or rupture of the membrane *etc.*) or associated filtration system (compromised glue lines or O-rings, broken mechanical seals, *etc.*). The integrity loss occurring at the membrane surface is further classified into that caused by physical (shear stress and vibrations) or chemical (oxidizing agents) factors.

In industrial settings, membrane deterioration is caused by oxidizing agents (i.e., hypochlorite), for example, contained in the upstream water of RO membranes to mitigate biofouling.[20,21] The oxidizing agents degrade polyamide layer and impair the performance of salt and virus rejection.[22,23] In fact, oxidation was one of the most common reasons for membrane failure of seawater RO membranes[24] and estimated to be one of the most likely sources of damage to RO modules in wastewater reclamation.[22] However, this deterioration mechanism is not likely to explain the low quality of the RO treated water reported in the previous studies.[18,19] This is because their feed water contains no chlorine (groundwater[18]) or little (tap water, whose chlorine concentration declined to less than 0.1 ppm possibly due to household water storage[19]). Hence, other cause is strongly suspected. To the best of our knowledge, no study has investigated the mechanism of deterioration of residential RO.

The intermittent operation of residential RO can be a cause of membrane deterioration, since it leads to repeated pressurization, which in turn loads frequent shear stress on the membrane element. In fact, Wang et al. pointed out that pressurization and de-pressurization move the feed spacer of the spiral-wound RO element which damages the membrane surface.[25] Hence, the impact of repeated pressurization on the removal performance of residential RO membrane should be investigated.

For evaluating the loss of integrity of RO membrane, virus removal is an appropriate indicator in two aspects. Firstly, viruses are one of the major microbial contaminants in drinking water.[26] Additionally, viruses are more difficult to be removed by membranes than other types of pathogens (i.e. bacteria and protozoa) because their size (30 – 100 nm) is smaller than bacteria and protozoa (micrometer in size). The size of the virus allows for detecting the integrity loss of the membrane with high sensitivity. In fact, previous membrane filtration studies have shown that the removal efficiency of viruses were lower than that of bacteria.[27–29] Generally, the virus removal is not complete even by intact RO because of abnormally large pores[30] or compromised O-ring sealing.[31,32] The $\log_{10}$

removal of virus by intact polyamide RO membranes were reported to be from 2.7 to > 6.7 depending on the water quality, membrane configuration and manufacturers.[23,33,34]

Bacteriophages have been used extensively in filtration studies as a surrogate for waterborne viruses because of their morphological and structural similarity.[5,35] For example, previous studies evaluated virus removal by membranes using bacteriophage MS2,[22,23,33,34,36] while other studies have used φX-174.[37–39] Although these bacteriophages are approximately the same in size (MS2: 23–25 nm, φX-174: 27–33 nm), their surface characteristics are different. First, MS2 has a larger negative surface charge than φX-174 at neutral pH. Additionally, MS2 is more hydrophobic than φX-174.[40] Electrostatic and hydrophobic interactions between membranes and viruses play a crucial role in determining virus removal efficiency[35] even though size exclusion is the predominant mechanism of virus removal.[5] Therefore, the use of the two surrogates is preferable to avoid overestimation of the virus removal efficiency of membranes. In fact, WHO recommends the use of both MS2 and φX-174 to evaluate virus removal by household water treatment technology.[41]

The aims of this study were (i) to evaluate the impact of repeated pressurization on virus removal by RO membrane for household water treatment, and (ii) to determine the location of integrity loss caused by repeated pressurization so as to understand the mechanism of deterioration.

Table 1 Comparison of typical features of residential RO and industrial RO
The information about industrial RO membrane is cited from Greenlee et al.[2]

	Residential RO	Industrial RO	
Purpose	Household water treatment	Wastewater reclamation	Desalination
Salt removal	> 93 %	95–99%	> 99.4–99.7 %
Permeability	High	Medium	Low
Replacement frequency	-	5–7 years	2–5 years
Surface Area	< 1 m^2	3–40 m^2	
Operation	Intermittent	Continuous	
Maintenance	None	Chemical cleaning and flushing	

2. Materials and methods

2.1. Preparation and quantification of bacteriophage MS2, φX-174, and *E. coli*

Bacteriophage MS2 and φX-174 were propagated using *E. coli* K12A/λ(F^+)[42] and *E. coli* C (NBRC 13898) as host strains. After propagation, the phage suspensions were centrifuged at 5,000 g for 15 min and filtered through a cellulose acetate filter (0.2 μm, DISMIC-25CS, Advantec, Tokyo, Japan). The filtrate was concentrated using a Centriprep YM-50 filter unit (Merck Millipore, Tokyo, Japan). The titers of the obtained phage stock solutions were approximately 10^{12} and 10^{10} PFU/mL for MS2 and φX-174, respectively. Then, the phage suspensions were further purified as follows.

Ultracentrifugation was performed at 59,000 g for 6 h to pelletize the bacteriophages. Then, the pellets were resuspended in 4 mL of TE buffer (Tris-HCl: 10 mM, EDTA: 1mM, pH 7.4, TaKaRa, Shiga, Japan). The phage suspension obtained was then purified by density gradient using iodixanol (60% OptiPrep; Axis-Shield, Dundee, Scotland). Briefly, approximately 3 mL of 40% iodixanol solution prepared in TE buffer was placed in an ultracentrifuge tube. Subsequently, 2 mL of 20% iodixanol prepared in the obtained phage suspensions was layered on the 40% iodixanol solution. Then, the prepared tubes were centrifuged at 160,000 g for 7 h at 20°C.

After centrifugation, a total of ten aliquots (500 μL each) were sequentially removed from the top of the tube by pipetting. An aliquot corresponding to the position of each

phage was dialyzed twice against 500 mL of MilliQ for approximately 12 h each and then against 500 mL of TE buffer for 18 h using a Float-A-Lyzer device (MW 100 kD; Spectrum Laboratories, Inc., Rancho Dominguez, CA, USA). MS2 and φX-174 phage were then recovered and stored at 4°C prior to further experiments. Using this purification method, 10^{11} (MS2) and 10^{10} (φX-174) PFU/mL of bacteriophage stocks were obtained. MS2 and φX-174 were quantified by plaque assay (double agar layer method) The same strain of *E. coli* that was used for bacteriophage propagation was used as host bacteria.

E. coli IFO3301 was incubated at 37 °C overnight in Luria–Bertani broth and then washed three times with phosphate buffer solution (1/15 M, pH 7.2, Wako, Japan). The *E. coli* concentration in the obtained stock was approximately 10^8 CFU/mL. The stock was stored at -80°C until further experiments. The number of *E. coli* was determined by colony-forming unit (CFU) assay with Chromocult agar, according to the manufacturer's recommendations (Merck Millipore).

2.2. RO membrane and accelerated fatigue test

A spiral-wound element with polyamide thin-film composite (TFC) membrane (active membrane area: 0.46 m^2, TW30-1812-50, Dow Filmtec, MN, USA) was used for the accelerated fatigue test. According to the manufacturer,[43] salt removal by this membrane is more than 96% under the following test conditions: softened tap water (TDS: 250 mg/L), 25°C, 15% recovery, 3.4 bar. The maximum operating pressure is 10 bar. Also, the manufacturer warranted that this membrane can be used for three years unless improper operation or maintenance.

An accelerated fatigue test consists of two parts: repeated pressurization and evaluation of virus removal. As the filtration apparatus, a commercially available one (Kangaroo, Taiwan) in a POU shop in Hanoi, Vietnam, where RO-POU is widely installed in households, was used to mimic actual household use conditions. The apparatus consists of tubes, pump, membrane housing, and retentate flow restrictor. The accelerated fatigue tests were performed in triplicate (i.e. Run 1, Run 2, Run 3). Before each run , a virgin TFC membrane was installed in the housing according to the manufacturer's guideline. Then, 10 L of deionized (DI) water was filtered to rinse the entire filtration system.

2.2.1. Repeated pressurization

The membrane was repeatedly pressurized in a closed loop system as shown in Figure 1A. Repeated pressurization was performed by turning on and off the pump, which is a component of the RO-POU, using 5 L of DI water as the feed water. The pump was turned on for 10 seconds (pressurization) and turned off (de-pressurization) for 20 seconds; this

repeating process was controlled by a periodic timer (FT-011, TGK, Tokyo, Japan). The maximum feed pressure was kept at 5.5 ± 0.2 bar. The flow rate was 0.72 – 1.2 L/min. This setting allows for simulating the intermittent operation in households and observing the impact of repeated pressurization in the shorter term. After predetermined cycles of pressurization and de-pressurization (Figure 1B), the system was stopped for virus removal test. The controls of pressurized time and maximum pressure were confirmed by recording the pressure (GC61, NAGANO KEIKI, Tokyo, Japan) at the outlet of retentate every second during repeated pressurization as shown in Figure 2. Interestingly, this operation has led to a gradual change in the observed pressure response; the system needed less time to reach the max pressure (i.e. 5.5 bar) and to depressurize as the number of cycles increased. This might be because the recorded pressure depends not only on the pump but also the membrane itself. Changes in membrane properties during the repeated pressurization (i.e., compaction and membrane deterioration) might cause such a phenomenon.

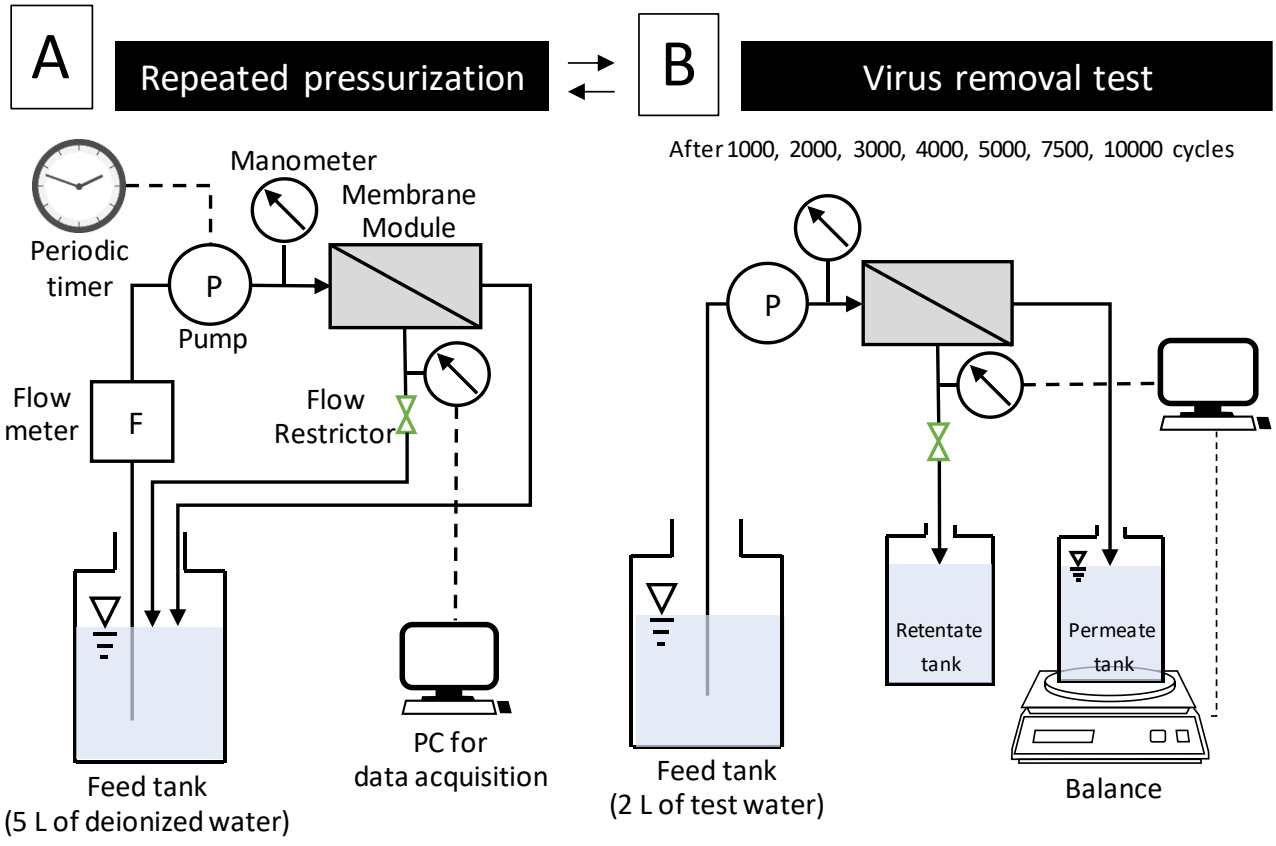

Figure 1 Schematic illustration of the filtration apparatus during accelerated fatigue test

Mode A shows the filtration settings during repeated pressurization while mode B shows those during virus removal test

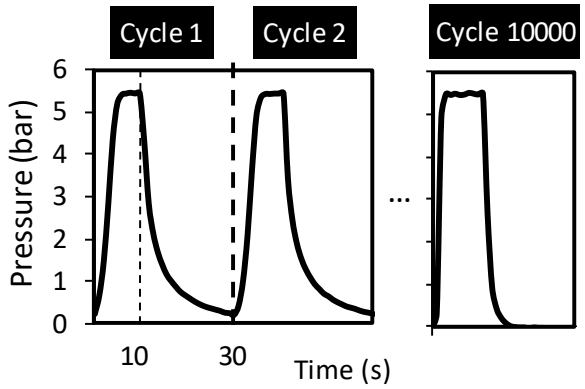

Figure 2 Profile of pressure on the feed side during repeated pressurization

2.2.2. Virus and *E.coli* removal test

After cycles of pressurization, the flow path of the filtration apparatus was transformed, as shown in Figure 1B to evaluate the virus removal efficiency. The entire filtration system was rinsed with 5 L of DI water prior to evaluation of virus removal, the permeate of which was used as negative control. During the rinse, the weight of the permeate was measured to obtain pure water permeability. The mass of permeate was monitored during filtration by an electrical balance (GX-4000, A&D, Tokyo, Japan). The permeability was normalized to 25°C.

A 20 μL aliquot of the purified MS2 and φX-174 was spiked into 2 L of general test water (GTW), which simulates high-quality water, such as groundwater or rainwater. The use of GTW for the evaluation of virus removal is recommended by WHO.[44] For preparing 2 L of GTW, sodium bicarbonate (410 mg), 2 M hydrochloric acid (440 μL), and tannic acid (3.7 mg) were added to DI water according to the WHO protocol. The water quality of the resultant GTW was as follows: temperature: 18–23°C, pH: 7.0–7.5, TOC: 1 mg/L, EC: 17.8–19.3 mS/m, alkalinity: 90–110 mg $CaCO_3$/L. The concentration of MS2 and φX-174 were 10^6 and 10^5 PFU/mL, respectively. Filtration was carried out at a constant pressure (5.5 ± 0.2 bar) in a cross-flow mode. After the filtration, the pH of the permeate became lower to 5.5 – 6.0 due to the dissolution of CO_2 to the permeate.

A total of 2 L of the first retentate and permeate were both returned to the feed tank to achieve a steady condition. After 1.8 L was filtered, the feed water and the permeate were collected and immediately analyzed for EC (WM-32EP, DKK-TOA, Tokyo, Japan). The remained samples were kept at 4°C and analyzed for microbial concentration within 12 h of collection. Finally, the entire filtration system was again rinsed with 5 L of DI water to flush out the remaining viruses. These procedures were conducted after 1,000, 2,000, 3,000, 4,000, 5,000, 7,500, and 10,000 cycles.

Following the testing of virus removal after 10,000 cycles, *E. coli* removal was also determined to assess the deterioration level of the repeatedly pressurized membrane. A 100 μL aliquot of purified *E. coli* was suspended in GTW, which was then used as feed water. The filtration and sample collection were conducted using the same method as that of the evaluation of virus removal. After the accelerated fatigue test, the RO membranes were soaked with DI water in a watertight container and kept at 4°C until further experiments.

The removal efficiency were quantified logarithmically as shown in Eq (1):

$$\text{Log}_{10}\ \text{removal} = -\log_{10}\left(\frac{C_p}{C_f}\right) \quad (1)$$

where C_p, EC or virus/*E.coli* concentration in the permeate and C_f, EC or virus/*E.coli* concentration in the feed.

2.3. Evaluation of virus and *E. coli* removal by constantly pressurized membrane

Constant pressurization was conducted by the filtration apparatus shown in Figure 1A. Contrary to the repeated pressurization, the periodic timer was kept turned on to pressurize the membrane continuously. The total filtration volume was approximately 1,500 L of DI water, which was equivalent to that in repeated pressurization. Virus removal was evaluated before and after the constant pressurization as described in 2.2.2. *E. coli* removal was also determined after constant pressurization.

2.4. Virus and *E. coli* removal in a flat-sheet configuration

To examine the integrity loss on the membrane surface, an autopsy of spiral-wound RO membranes was performed. Two pieces of flat-sheet membranes were obtained from each element and tested for removal of virus and *E. coli*. The tested membrane elements included those after repeated pressurization (n = 3), one after constant pressurization (n = 1), and a virgin membrane (n = 1). The obtained flat-sheet membranes were set to a dead-end cell unit (UHP 150K, Advantec, Tokyo, Japan). The filtration area of the cell was 159.6 cm^2, which was equivalent to 3.5 % of that of the spiral-wound element. Prior to the removal test, the filtration cells and tubes were rinsed with DI water. A total of 50 mL of permeate was collected as a negative control.

To evaluate the virus removal in flat-sheet configuration, 500 mL of feed water, prepared in the same way as described in 2.2.2, was added to the cell. The feed water was

pressurized by nitrogen gas at 5 bar, with stirring at 20 rpm (average cross-flow velocity: 0.1 m/s) to allow 50 mL of the feed water to pass through the flat-sheet membrane. After filtration, the remaining feed water and permeate were collected for plaque assay and EC measurement. *E. coli* removal was also evaluated using the same method as that used for virus removal test.

3. Results and discussion

3.1. Accelerated fatigue test

3.1.1. EC rejection and pure water permeability

Figure 3 shows the membrane performance (EC and pure water permeability) during repeated pressurization. At the beginning of the accelerated fatigue test, the rejection of EC gradually increased while pure water permeability decreased. EC rejection at 3,000 cycles (1.73 ± 0.09 $\log_{10}$ (98.1%) (mean ± SD)) was higher than that at 0 cycle (1.48 ± 0.06 $\log_{10}$ (96.7%)). Pure water permeability at 3,000 cycles (4.17 ± 0.02 L/h·bar·m^2) was lower than that at 0 cycle (6.04 ± 0.30 L/h·bar·m^2). This may be due to membrane compaction, as pressurization can cause compaction of the polymer layer of composite membranes,[25] which can block the passage of water molecules through polymeric membrane, thus resulting in a drop in water permeability[45] and an increase in observed salt removal.[46] These phenomena were also observed in constantly pressurized membranes. As shown in Figure 4, EC rejection increased, which corresponded to decreased permeability.

After 3,000 cycles, EC rejection was gradually decreased in all runs and reached 1.06 ± 0.37 $\log_{10}$ at 10,000 cycles. As shown in Figure 4, this value was significantly lower than that of the constantly pressurized membrane (one-way ANOVA, $p < 0.05$), which demonstrates that repeated pressurization deteriorated the EC rejection efficiency.

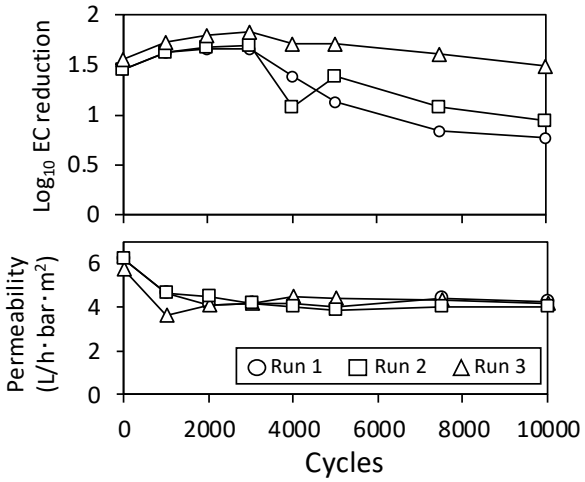

Figure 3 EC rejection and permeability during accelerated fatigue test

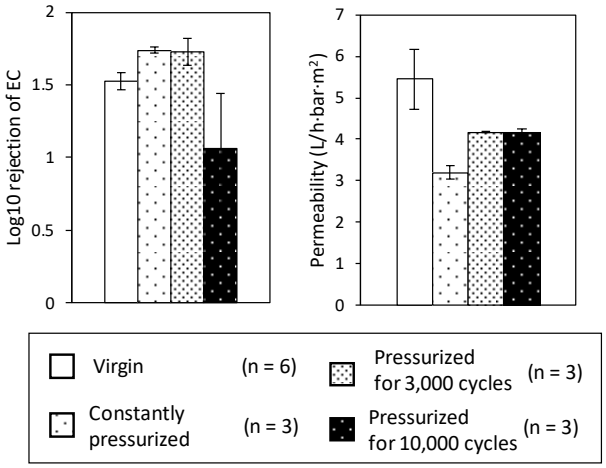

Figure 4 Performance of virgin, constantly pressurized and repeatedly pressurized (3,000 and 10,000 cycles) membranes

Error bars represent the standard deviation.

3.1.2. Profile of virus removal

The profile of virus removal during the accelerated fatigue test is shown in Figure 5 together with the *E. coli* removal at 10,000 cycles. In all runs, the removal of φX-174 was maintained at approximately 4 $\log_{10}$ for the first 3,000–5,000 cycles, followed by a dramatic decrease. After 10,000 cycles, the removal of φX-174 was 1.75 ± 0.31 $\log_{10}$.

The removal of MS2 fluctuated in Run 1 and Run 2. This might be attributable to the inactivation of MS2 due to osmotic pressure during storage of the permeate, whose EC was extremely low; in a previous study, bacteriophage MS2 was shown to be inactivated in ultrapure water by 2 $\log_{10}$ in 4 hours.[47] Hence, MS2 in the permeate might be inactivated, which overestimated the $\log_{10}$ removal. In Run 3, therefore, TE buffer was added into the permeate immediately after the challenge test to stabilize the EC, where the log removal of MS2 was stable and comparable to that of φX-174. For the following experiments, TE buffer was added into all samples to avoid possible inactivation of MS2.

It should be noted that *E. coli* (size: approximately 1 μm) was also detected in the permeate after 10,000 cycles in all runs. This suggests that the observed integrity loss at 10,000 cycles was of the order of micrometers in size.

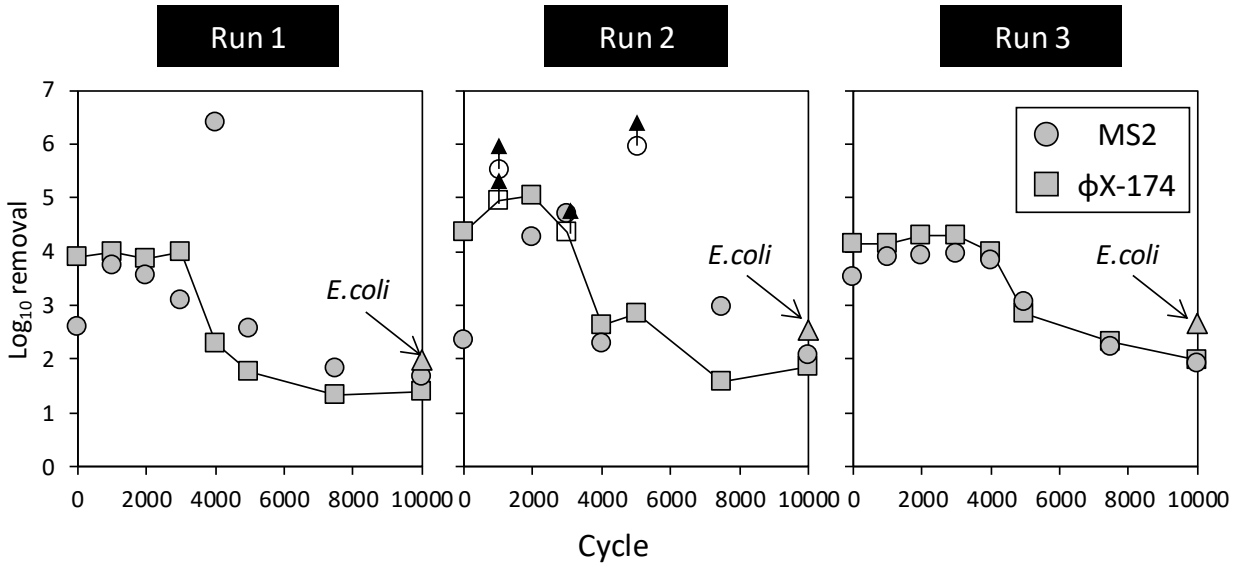

Figure 5 Virus removal performance during accelerated fatigue test and *E. coli* removal efficiency after 10,000 cycles

Unfilled points with arrows stand for unquantified results.

3.2. Comparison of EC, virus, and *E. coli* removal by constantly pressurized and repeatedly pressurized membranes

The membrane pressurized at constant pressure was also examined for virus and *E.coli* removal as a control. The total filtered volume of these membranes was the same as that of repeatedly pressurized membranes. Therefore, the impact of filtered volume on RO membrane can be offset between repeatedly pressurized and constantly pressurized membranes.

Figure 6 shows the EC, virus, and *E. coli* removal of the constantly pressurized membranes together with those of virgin ones and repeatedly pressurized ones (after 10,000 cycles) for comparison. Virus removal by constantly pressurized membranes was slightly better than that by virgin membranes; removal of MS2 and φX-174 by virgin membranes was 2.9 ± 0.4 $\log_{10}$ and 3.9 ± 0.4 $\log_{10}$, respectively (n = 6), while the removal efficiency increased to 3.7 ± 0.6 $\log_{10}$ and 4.1 ± 0.6 $\log_{10}$, respectively (n = 3) after constant pressurization. This result also may be explained by the membrane compaction. A previous report[48] has also observed the enhanced virus rejection by constant pressurization and attributed it to the possible morphological change of membranes. Hence, filtration of 1,500 L DI water at constant pressure itself did not impair the membrane performance in our experimental setting.

The removal of both MS2 and φX-174 by repeatedly pressurized membranes was significantly lower than that by constantly pressurized membranes (one-way ANOVA, *p*

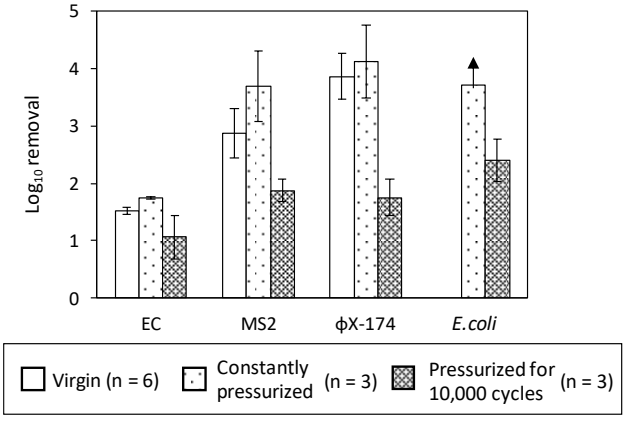

Figure 6 Removal performance of virgin, constantly pressurized and repeatedly pressurized (10,000 cycles) membranes

Error bars represent the standard deviation. Arrows indicate unquantified results.

< 0.05). Of note, all three data of MS2 removal by the repeatedly pressurized membranes were included in the statistical analysis despite the possible overestimation of $\log_{10}$ removal. This possible overestimation is liable to make the difference smaller, which does not lead to false-significant results of the statistical comparison. Also, the removal of *E.coli* by repeatedly pressurized ones were lower than that of constantly pressurized ones.

Consequently, the comparison between the two groups clearly indicates that repeated pressurization itself impaired the virus removal efficiency of the RO membrane. In our experimental settings, chemical agents were not used during accelerated fatigue tests. Therefore, the deterioration was induced by the physical stress during repeated pressurization.

3.3. EC, virus, and *E. coli* removal in flat-sheet configuration

The loss of integrity can be divided into two types; the first type is due to the deterioration of the membrane surface (pinhole, abnormally large pores or rupture of the membrane, *etc*.), while the other is due to the failure of the associated filtration system (compromised glue lines or O-rings, broken mechanical seals, *etc*.). Hence, distinguishing the two mechanism is important to analyze the cause of deterioration.

A comparison between the removal efficiency of virus and that of *E. coli* makes it possible to estimate the mechanism providing dominant contribution to the deteriorated removal performance. If the dominant integrity loss occurs by the failure of associated filtration system, the obtained permeate consists of the permeate of RO and the leakage of the feed water which is not passing through the membrane; therefore, the observed removal efficiency of virus and *E. coli* should be similar even though *E. coli* is 10–100 times larger than viruses in size. In our observations, however, removal performance of φX-174 was significantly lower (by 0.65 $\log_{10}$) than that of *E. coli* (Paired *t*-test, $p < 0.05$). Therefore, we can hypothesize that the loss of integrity occurred on the membrane itself, which mainly led to the deterioration of removal efficiency.

To confirm this hypothesis, the RO membranes used in 3.1 were analyzed in flat-sheet configuration. Although optical microscope and scanning electron microscope are common to visualize the deteriorated membrane morphology directly,[22,23] their observable fields of view are too limited to identify the localized damages. In this study, therefore, these methods were not adopted to check the presence of integrity loss on membrane surface. Instead, microbial challenge test, which can examine the wider area of the membrane surface, were applied to autopsied flat-sheets. In fact, this method is one of the direct integrity tests in industrial settings.[49]

Figure 7 shows the removal performance (EC, MS2, and *E. coli*) of the virgin, constantly pressurized, and repeatedly pressurized membranes in flat-sheet configuration. The performance in spiral-wound configuration is also presented for comparison. In Run 1 and Run 2, MS2 removal in flat-sheet configuration was comparable to that in spiral-wound configuration. Moreover, *E. coli* was detected in the permeate and their removal was also comparable to that in spiral-wound configuration. This strongly suggests the presence of leaks on the membrane surface. In addition, the comparability of the removal efficiency in both configurations indicates that the leaks on the membrane surface mainly decrease the virus removal of repeatedly pressurized membranes.

It should be emphasized that the EC rejection and MS2 removal of virgin and constantly pressurized membranes in flat-sheet configuration were comparable to those in spiral-wound. This suggests that the autopsy method in this work was conducted properly, without damaging the membrane surface.

Contrary to the results in Run 1 and Run 2, MS2 and *E. coli* removal was higher than those in spiral-wound configuration in Run 3. Especially, *E.coli* was not detected in the permeate. Of note, the surface area of one piece of flat-sheet is 3.5% of the overall spiral-wound element. Hence, our method, evaluating the microbial removal of two pieces of flat-sheets, allows for examining the integrity of only 7% of total surface area of one spiral-wound element. Therefore, this result still could not exclude the possibility of the integrity loss on the membrane surface. In fact, the MS2 removal in Run 3 was still significantly lower than that by the constantly pressurized membrane (one-way ANOVA, $p < 0.01$). This implies that the membrane surface also deteriorated in Run 3.

In this study, the integrity loss of associated filtration system was not investigated. Hence, it is impossible to discuss its integrity. However, the results indicate the loss of integrity on the membrane surface and its substantial contribution to deteriorated virus removal by repeatedly pressurized membranes.

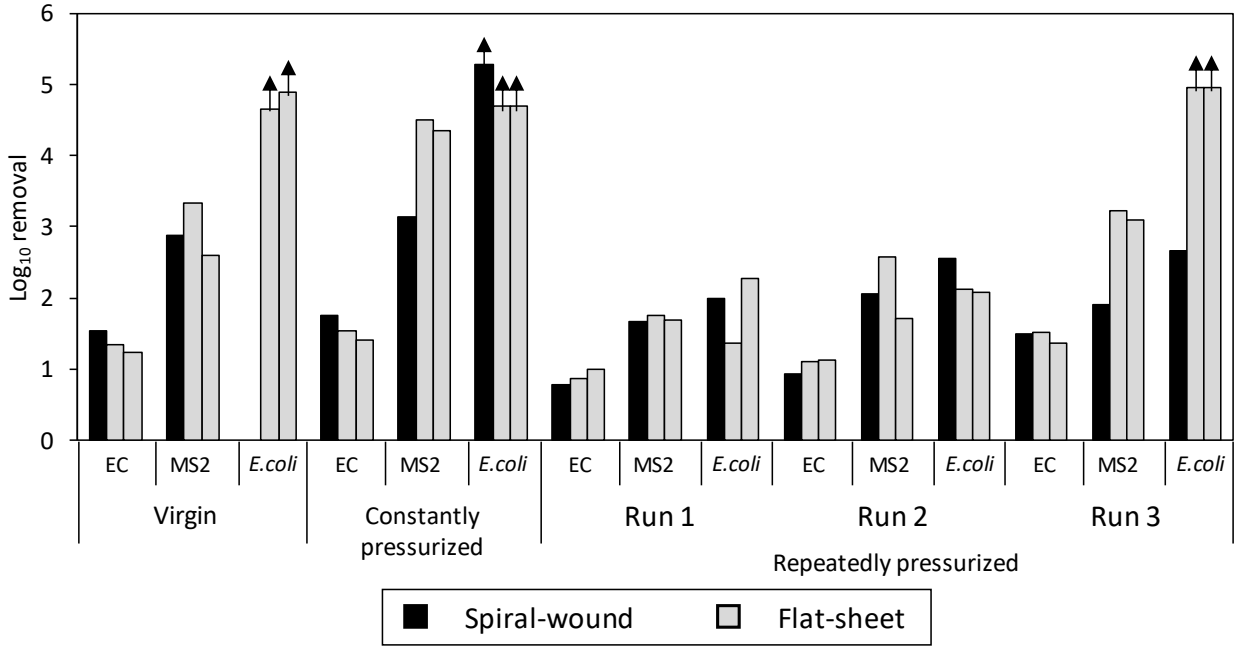

Figure 7 Removal performance in flat-sheet configuration

Arrows represent unquantified results.

One possible mechanism of the deterioration of membrane surface was excessive shear stress during pressure transients on the feed spacer, which caused indentations on the membrane surface. In spiral-wound configuration, flat-sheet membranes are sandwiched between feed channel spacers and permeate collection materials, and these are rolled around the permeate tube.[25] The feed channels constrict the flow path, which aggravates the shear stress in spiral-wound membranes. Hence, the distribution of shear stress is not uniform.[50] In other words, membrane surfaces in some regions are exposed to relatively large amounts of localized stress, even when the membrane is operated at low pressure. A recent study suggests that even modest applied pressure (1–2 bar) may cause membrane indentations, which possibly damages the membrane surface at the point of spacer-membrane contact.[51] Moreover, a previous review paper[25] has pointed out that the cycle of pressurization and de-pressurization moves the feed channel spacer relative to the membrane, which may damage the membrane surface. Overall, it is hypothesized that inertial forces during pressure increase accelerated the membrane indentations, which led to the deterioration of membrane surface. However, the hydraulic aspects during pressure

transients should be studied in the future to elucidate the mechanism of the deterioration caused by repeated pressurization.

3.4. Implications of maintenance strategy for RO membrane for household water treatment

Repeated pressurization was shown to cause integrity loss on the membrane surface, which mainly deteriorated the virus removal performance of the RO membrane. This deterioration mechanism is presumably unique to household water treatment because of its intermittent operation. No study has paid attention to the unique susceptibility of residential RO membrane. This implies that the conventional maintenance method is not applicable for household use. Therefore, there is a need to develop maintenance guidelines considering their operational characteristics.

Firstly, the appropriate frequency of membrane replacement is discussed. Membrane replacement is the only applicable option in households. WHO requires POU devices to remove both MS2 and φX-174 by more than 3 $\log_{10}$ to reduce the health risks associated with drinking water by less than 10^{-4} DALYs/person/year.[41] Our results showed that virus removal is decreased to less than 3 $\log_{10}$ after 3,000–5,000 cycles of pressurization (Figure 5). This result suggests that membrane replacement should be conducted after 3,000 cycles of pressurization. As reported by a paper, which conducted a questionnaire survey about RO-POU usage, this device is used for cooking and drinking purposes.[12] Assuming that the membrane is pressurized ten times a day, RO membranes need to be replaced almost every year. On the other hand, RO membranes for brackish water (BWRO) can be used for up to 7 years[2] or 10 years[23] in industrial settings. This suggests that the frequency of membrane replacement in households is much higher than that in industrial settings. Moreover, RO membranes should be replaced more frequently if the device is used more often. Therefore, we recommend inclusion of the number of times of pressurization on RO membrane as a criterion to determine the frequency of membrane replacement in addition to the conventional criteria, such as the age of membrane or total filtration volume.

Furthermore, we suggest countermeasures to mitigate the impact of repeated pressurization on the membrane surface. The pressure increasing rate, which depends on the time required for the pressure to increase from zero to the maximum working pressure, affects the mechanical response of RO membrane.[25] Therefore, it may be recommended to install valves and pumps that reduce the pressure shock and vibrations in RO-POU devices. In a previous study[52], installation of slow valves and pumps with slow starts and

slow stops were shown to elongate the lifespan of the UF membrane used in a wastewater treatment facility. In this study, we did not analyze the effect of such valves on the mitigation of the damage caused by repeated pressurization. However, these approaches probably work well considering that constant pressurization does not lead to deterioration.

In future work, there is a need to investigate whether repeated pressurization can be involved in the deterioration of other commercially available RO membranes. Furthermore, it is of special importance to analyze the membranes used in actual household operations to evaluate the contribution of repeated pressurization to membrane deterioration because other factors, such as biofouling and oxidized damages by chlorine in tap water, possibly cause the deterioration.

4. Conclusions

This study focused on the impact of repeated pressurization on virus removal efficiency of RO membranes for household water treatment. This study showed that: i) repeatedly pressurized membranes rapidly deteriorates compared to constantly pressurized ones; ii) the deterioration is mainly due to the loss of integrity of the membrane surface of RO membranes.

RO membranes for household water treatment are exposed to repeated pressurization because of their intermittent operation. Therefore, the number of times that the RO membrane is pressurized should be included as a criterion to determine the frequency of membrane replacement in addition to the conventional criteria, such as the age of membrane or the total filtration volume.

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Conflict of interest

The authors declare no conflict of interest.

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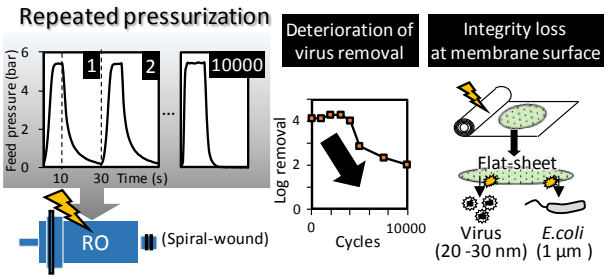

Repeated pressurization caused integrity loss at the surface of reverse osmosis membrane resulting in a dramatic decrease in virus removal