Regeneration of solid phase filter by chemical cleaning

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Abstract : Recently, separation membranes have been applied to fields such as water supply, sewage treatment, gray water reuse, and air pollution control. Chemical cleaning technology is attracting attention among the methods of reusing these expensive separation membranes. It was found that the separation membrane could be regenerated using chemical cleaning. Specifically, it was found that the use time of the separation membranes regenerated by chemical cleaning was sustainable for more than 1,700 hours. Additionally, it was found that the flux recovery ratio after chemical cleaning was maintained at least 60%. In addition, the flux recovery ratio of HYDREX 4710, an organic membrane cleaner, and 4703, an inorganic membrane cleaner, was 76% and 62%, respectively, showing the highest flux recovery ratio among the chemicals used. Considering that the target raw water of this study is biological secondary treatment water, it was suggested that chemical cleaning could be actively used to regenerate separation membranes in future water treatment.

Keywords: Chemical cleaning, specific flux, solid phase filter, regeneration, transmembrane pressure.

1. Introduction

Sand filtration is still mostly used in the drinking water production process in Korea, but it is gradually being replaced by membrane filtration [1-2]. In addition, most research institutes' laboratories, university laboratories, and public or private analytical institutions use large quantities of solid phase filters to produce ultrapure water and pure water. When these membranes and solid-phase filters are used for a certain period, various contaminants accumulate in the membrane or solid-phase filter, leading to rapid deterioration (a state in which the membrane or solid-phase filter can no longer be used due to a decrease in the quality of the filtered water) thus they must be replaced. Companies performing analysis work also use large amounts of expensive membranes to collect polluted air when analyzing air quality, and also consume many solid phase filters in manufacturing pure and ultrapure water. Contaminants are adsorbed on used solid filters, which causes environmental pollution when disposed of inappropriately [3-5]. Meanwhile, the most critical factor in using a solid filter is its life. The life of the regenerated solid filter directly

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affects the increase in analysis costs. Also, it affects the accuracy of analysis as it is used for atmospheric analysis or preparation and dilution of reagents. Contamination of solid phase filters is a very complex mechanism in which physical, chemical, and biological factors interact in combination. Membranes or solid-phase filters for drinking water have very different characteristics from those for gray water or ultrapure water [6]. As for domestic related technologies, various cleaning agents have been studied through laboratory and field experiments to remove pollutants from membranes or solid filters, most of which are regeneration methods through backwashing. Specifically, the focus is on the pressure during backwashing, cycle, the amount and speed of washing water, etc. Foreign related technologies include conducting research on the design of membrane modules and optimization of supply flow rate by analyzing the phenomenon of movement of suspended solids contained in raw water on the surface of the membrane when it flows between the pores of the membrane or solid phase filter from a hydrodynamic perspective. It has been done. in addition, when inorganic substances dissolved in an aqueous solution exceed their solubility during the process of concentration in a solid column, they form colloidal precipitates and accumulate on the surface of the solid phase filter by systematically analyzing the effects of colloid size and electrical characteristics on contamination. This decreasing phenomenon of membrane permeability has been studied. Since the contamination phenomenon of organic substances is determined by the physical/chemical affinity between the contaminants and the solid filter material, several research teams are conducting research to develop solid filter materials suitable for specific solutions. In particular, a method of introducing a functional group to suppress contamination on the surface of an existing solid filter is being used [7-10].

Therefore, in this study, we intend to apply chemical cleaning to regenerate relatively expensive solid filters. In order to maximize the regeneration effect of the solid-phase filter using chemicals (desorption and decomposition of contaminants adsorbed on the solid-phase filter), a solvent or oxidizing agent is added. The cleaning agents used for chemical cleaning were oxidizing agents, alkaline agents, and membrane-specific detergents previously used for membrane regeneration. To check how well the regenerated solid filter maintains its original performance, various methods, such as transmembrane pressure, were applied.

2. Experimental methods

The processing capacity of the membrane filtration device used in this study was 3L/hr, and it consisted of a casing module equipped with a hollow fiber ultrafiltration membrane made of PES with a molecular cutoff of 30,000Da. The length of the module is 370mm, the diameter is 25mm, and the membrane area is $0.045m^2$. Biological secondary treatment water was used as raw water, and the entire process was structured to allow automatic and manual operation. The outline diagram of the process is shown in Fig. 1.

The specifications and operating conditions of the membrane used in the experiment are summarized in Table 1. The material of the membrane used in the experiment was polyether sulfone, which is the most commonly used material among organic membranes. The A-1 and A-2 series membranes used in this study differ in the content of polyether sulfone [11]. The pore size of the membrane has a molecular cutoff of 30,000, and the membrane area is $0.045m^2$. Secondary treatment effluent from the G sewage treatment plant was used as the membrane feed water. It was pretreated using a filter with an average pore size of 200 μm to remove coarse particles before being
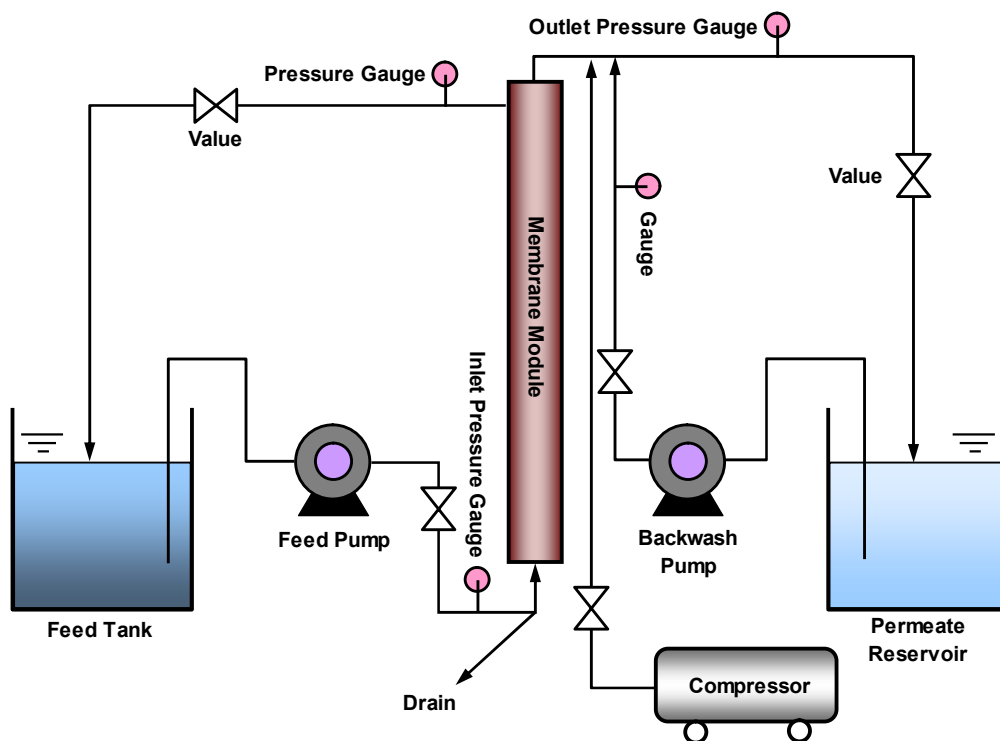
Fig. 1. Configuration diagram of membrane filtration device.

Table 1 Membrane and operation conditions

Item		Specification
Membrane	MWCO	30,000Da
	Material	Polyether sulfone
Module	Surface area	0.045m^2
	Material	Polyvinyl chloride
Operation	Flux	0.8m^3/m^2/d
	Filtration	120 min
	Backwash(water+air)	20 min(water 15 min + air 5 min)

supplied to the raw water tank. The feed water from the raw water tank is mixed with circulating water and supplied to the membrane module. Raw water is supplied to the inlet of the membrane at a flow rate of 100mL/min using a metering pump (JP-100, Jenie Well), of which 50% (50mL/min) is filtered as permeate water. The remaining 50% returned to the raw water tank as concentrated water (circulating water) through cross-flow. During operation, the flux was operated at a constant flow rate of 1.6m^3/m^2/d, and backwashing was performed for 20 minutes after 120 minutes of filtration. Of the 20 minutes of backwashing time, water backwashing using permeated water was performed for 15 minutes, and air cleaning using compressed air was performed for the

remaining 5 minutes. Chemical cleaning with chemicals was performed by separating the membrane module when the membrane differential pressure reached 100kPa.

The chemical cleaning treatment of the filtration membrane was performed when the membrane differential pressure reached 100kPa. The membrane module was separated, and the membrane module was immersed in a chemical washing tank for a certain period to perform chemical cleaning. To examine the cleaning effect of chemicals, nitric acid, and citric acid were used as acids, H_2O_2, and sodium hypochlorite were used as oxidizing agents and sodium hydroxide was used as an alkaline agent. Additionally, the effectiveness of HYDREX 4710 (Veolia Water), an organic membrane-specific cleaner, and HYDREX 4703 (Veolia Water), an inorganic cleaner, were compared with existing chemicals [12].

The flux recovery ratio to evaluate the effect on membrane cleaning was calculated as follows.

Here, $flux_{spec}$ represents flux corrected for water temperature and membrane differential pressure, $flux_{obs}$ represents measured flux, μ_{obs} represents the viscosity of water, μ_{25}

75 hours later, the transmembrane pressure rapidly increased to 20kPa. After that, the transmembrane pressure was almost constant at around 20kPa for up to 300 hours. Afterward it gradually increased until 400 hours, and after 400 hours, the membrane differential pressure rose again rapidly, reaching a membrane differential pressure of 100kPa 600 hours after the start of operation. The membrane module was separated and chemically cleaned with HYDREX 4710, an organic cleaner exclusively for membrane cleaning. After the first chemical cleaning, the transmembrane pressure tended to decrease to 24kPa; at this time, the transmembrane pressure was found to have recovered to 76%. Unlike the first operation, the change in membrane differential pressure after 600 hours of operation showed a tendency for the membrane differential pressure to rise immediately. The second chemical cleaning was performed 1,000 hours after the start of the operation, and the membrane pressure increased to 100kPa after 400 hours of operation after the first membrane cleaning. The second chemical cleaning was performed using HYDREX 4703, an inorganic cleaning

$$\text{Flux recovery rate}(\%) = \frac{\text{Flux}_{spec} \text{ after chemical cleaning}}{\text{Initial flux}_{spec}} \times 100$$

$$\text{flux}_{spec} = \text{flux}_{obs} \times \left(\frac{\mu_{obs}}{\mu_{25}}\right) \times \left(\frac{100kPa}{TMP_{obs}}\right)$$

represents the water viscosity at 25℃, and TMP_{obs} represents the measured membrane differential pressure.

3. Results and discussion

The change in transmembrane pressure of the A-1 series during the operation period is shown in Fig. 2. At the start of the operation,

agent. After chemical cleaning, the transmembrane pressure was 38kPa, higher than that of organic cleaners. At this time, the membrane differential pressure recovery ratio was 62%, and the recovery ratio was 14% lower than that of the first chemical cleaning. The third chemical cleaning was performed 1,335 hours after the start of the operation, and the membrane differential pressure after the third chemical cleaning was 26kPa, which

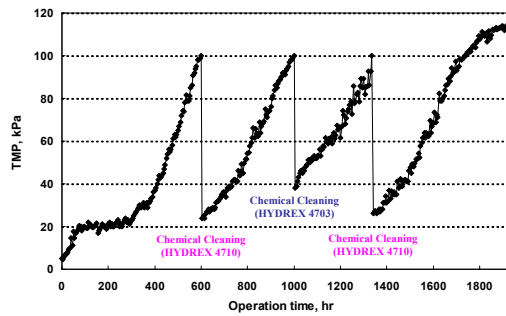was almost similar to the membrane differential pressure after the first chemical cleaning.

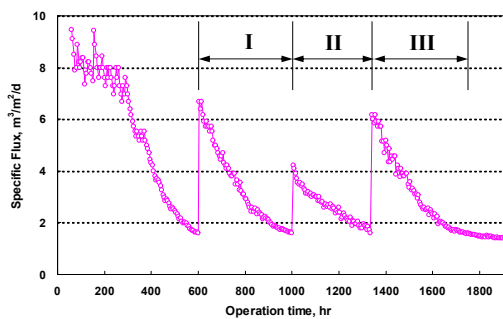Fig. 2. Changes in transmembrane pressure (A-1 series).

Fig. 3. Correction flux change (A-1 series).

Fig. 3 shows the change in corrected flux for a water temperature of 25℃ and 100kPa. The corrected flux just before the first chemical cleaning was $1.60m^3/m^2/d$, but after the chemical cleaning, the corrected flux increased to $6.67m^3/m^2/d$. After the second chemical cleaning, the corrected Flux was $4.21m^3/m^2/d$, and after the third chemical cleaning using the same organic cleaner (HYDREX 4710) as the first chemical cleaning, the corrected Flux increased again to $6.15m^3/m^2/d$. The operating time required for the corrected flux to decrease to $1.60m^3/m^2/d$ after the first chemical cleaning (organic cleaning agent) was about 400 hours (section I). The time taken for the corrected flux to decrease to $1.60m^3/m^2/d$ after the second

chemical cleaning (inorganic cleaning agent) (Section II) was found to be approximately 350 hours. After the third chemical treatment, the time it took for the corrected flux to reach $1.60m^3/m^2/d$ (Section III) increased to about 400 hours. This experiment found that organic cleaners had a higher flux recovery ratio and longer operating times until chemical cleaning than inorganic cleaners.

Fig. 4 shows the change in membrane differential pressure (A-2 series) when nitric acid, citric acid, hydrogen peroxide, sodium hypochlorite, and sodium hydroxide were used as membrane cleaning solutions. Fig. 5 shows the correction flux change. To examine the cleaning effect of individual chemicals, the stock solution was diluted to 2% and used. When the membrane differential pressure reached 100kPa, the membrane module was separated and immersed in the cleaning solution for each chemical for 2 hours, then diluted with distilled water to prevent the chemicals from remaining on the membrane surface and washed several times with distilled water until the pH of the washing solution became neutral.
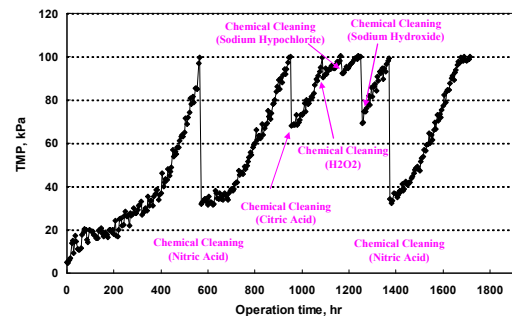

Fig. 4. Changes in transmembrane pressure (A-2 series).

About 565 hours after the start of operation, the transmembrane pressure reached 100kPa; at this time, the first chemical cleaning was performed using nitric acid. After chemical cleaning, the membrane differential pressure was lowered to 32kPa, and the

corrected flux was 5.00m³/m²/d. 385 hours after the first chemical cleaning (section I), the membrane pressure differential again reached 100kPa, and at this time, citric acid was used for the second chemical cleaning. After secondary chemical cleaning using citric acid, the membrane differential pressure was lowered to 68 kPa, and the corrected flux was 2.35m³/m²/d. The third chemical cleaning was performed 135 hours (section II) after the second chemical cleaning. At this time, the chemical used was hydrogen peroxide, and the membrane differential pressure after cleaning was 90kPa, which showed that the chemical cleaning effect was minimal. The fourth chemical cleaning was performed 80 hours (section III) after the third chemical cleaning. Sodium hypochlorite was used for the fourth chemical cleaning, and the transmembrane pressure after chemical cleaning was 92kPa. 85 hours after the 4th cleaning (section IV), the 5th cleaning used sodium hydroxide. When sodium hydroxide was used, the transmembrane pressure was lowered to 69 kPa, and the corrected flux also increased to 2.31m³/m²/d, 6 The chemical cleaning time until car washing also increased to 120 hours (section V). After sodium hydroxide, chemical cleaning was performed again using nitric acid. Because the effect of chemical cleaning using nitric acid may vary depending on the change of chemical and the cleaning order, the flux recovery ratio was investigated using the same chemical to examine this. In the 1st and 6th chemical cleaning, the membrane differential pressure decreased from 100kPa to 32kPa for the 1st chemical cleaning. In the 6th chemical cleaning, the membrane differential pressure decreased from 100kPa to 34kPa, so regardless of the cleaning order, the recovery of the membrane differential pressure required chemicals. It was judged to be more dependent on the type of chemicals rather than the order.

When using a membrane, the usage time of the membrane is determined by the backwash efficiency and the flux recovery ratio according to chemical cleaning, so reviewing the flux recovery ratio according to chemical cleaning is a very important economic factor in the use of the membrane [13-14].
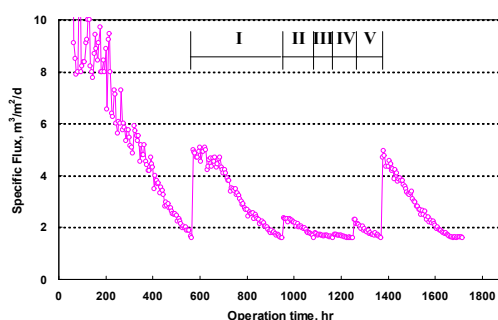

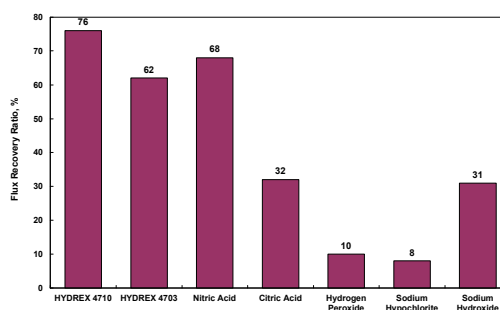Fig. 5. Correction flux change (A-2 series).

Fig. 6. Comparison of flux recovery ratio according to each chemical cleaning method.

Fig. 6 summarizes the membrane cleaning effects of individual chemicals. For individual drugs, the flux recovery ratios for citric acid, hydrogen peroxide, sodium hypochlorite, and sodium hydroxide were found to be low. These results mean that although organic substances present in water affect membrane contamination, there is also a significant amount of membrane contamination caused by inorganic substances.

Nitric acid showed a good flux recovery ratio of 68%. HYDREX 4710 and 4703, commercially available membrane cleaners, showed flux recovery ratios of 76% and 62%, respectively. Although the flux recovery ratio when using citric acid is about 32% due to the quality of the raw water used in this study, considering the low toxicity and high price competitiveness of citric acid, it can be used with nitric acid and HYDREX series cleaners.

4. Conclusions

This study attempted to regenerate the solid phase filter using various chemicals. The advantage of chemical cleaning is that the cleaning method is simple and does not require complicated equipment. It is a more environmentally friendly recycling method because there are no hazardous substances or an environment harmful to workers during recycling. The following conclusions were obtained:

1. It was found that the separator regenerated by chemical cleaning could last for more than 1,700 hours.

2. The results of a chemical regeneration experiment using two types of solid membranes (polyether sulfone series) showed a stable flux recovery ratio of over 60%.

3. Nitric acid as a cleaning agent showed a good flux recovery ratio of 68%. Nitric acid is inexpensive and has low toxicity, so it is considered suitable as a cleaning agent.

4. Currently commercially available organic membrane cleaners HYDREX 4710 and inorganic membrane cleaners showed flux recovery ratios of 76% and 62%, respectively, showing the highest flux recovery ratios among the chemicals used. Organic chemicals showed a better flux recovery ratio than inorganic chemicals.

5. Considering that the target raw water of this study is biological secondary treatment water, it was suggested that chemical cleaning can be actively used to regenerate solid filters in future water treatment.

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