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Effect of chemical cleaning conditions on the flux recovery of fouled membrane

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ABSTRACT

Flux recovery through chemical cleaning was investigated using small-sized membrane modules for application in drinking water treatment using river water as feed. This study focused on the causes of membrane fouling by evaluating the cleaning efficiency with several chemical agents at various conditions. Sodium hypochlorite and sodium hydroxide as basic chemicals, and citric acid, nitric acid, oxalic acid, and sulfuric acid as acidic chemicals were used in the experiment. Each chemical was prepared at concentrations of 0.1, 1, 3, and 5%. The mini-module was made of four strings of polyvinylidene fluoride hollow fibers with pore diameter of 0.038 μm. Flux was tested at constant pressure of 0.5 bar. The experiment was operated at the temperature range of 18.1–25.3°C. To compare the effect of water temperature, cleaning test was performed at the range of 0–5°C. Also, the effect of combination of chemicals was tested with cleaning sequences of base–acid–base and acid–base–acid. The surface characteristics of the membrane were also investigated using Scanning electron microscopy and tensile strength analyses. Prior to the chemical cleaning, flux of fouled membrane was measured using deionized water. Duration of chemical cleaning was set at 30 min, 1, 2, and 4 h, and then, the flux was checked. For the control, pure water flux was measured using virgin hollow fiber membranes. Among the chemicals, sodium hypochlorite showed the highest flux recovery rate of 44.0% at 1% concentration. On the other hand, for the acidic chemicals, the highest was only 38.1% recovery rate at 1% oxalic acid. Recovery efficiency increased as the concentration of chemicals and cleaning time increased. Organic or biofilm was considered as the main foulant as observed from the experimental results. In addition, the cleaning efficiency was better in basic than acidic.

Keywords: Chemical cleaning; Fouling; Hollow fiber membrane; Microfiltration; Flux; Recovery rate

1. Introduction

One of the most difficult parts in membrane filtration process faced by water purification plants is cleaning the fouled membrane. Primary foulants include organic pollutants, inorganic pollutants, and natural organic matter (NOMs). Physical cleaning is the easiest way in removing membrane foulants, such as backwashing and air scrubbing [1–5]. However, it

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was observed that the flux recovery rate does not increase as much after performing physical cleaning [1]. Thus, chemical cleaning should be applied in removing organic and inorganic foulants as well as NOMs effectively. It was proven that the chemical cleaning using suitable cleaning agents enhances the flux recovery rate [1,6].

Chemically enhanced backwashing (CEB) and cleaning in place (CIP) are two common methods of chemical cleaning. CEB is executed for a certain period of time every day, while CIP is usually done twice a year in a 6-month interval if physical cleaning and CEB do not work to recover the efficiency of membrane. Besides the cleaning frequency, CEB also differs from CIP in cleaning time and cleaning agent concentration [6].

In chemical cleaning, sodium hydroxide (NaOH) and sodium hypochlorite (NaOCl) are mainly used as alkaline agents, and sulfuric acid (H_2SO_4), citric acid ($C_6H_8O_7$), nitric acid (HNO_3), and oxalic acid ($C_2H_2O_4$) as acid agents under the category of organic/inorganic acid, which are used in CIP [6–15].

The aim of this study is to find the appropriate cleaning agent for optimizing the flux recovery rate. Two parameters were considered, concentration of cleaning agents and chemical cleaning time. Four cleaning agent concentrations were investigated (0.1, 1, 3, and 5%).

Tensile strength is measured to analyze the effect of the cleaning agent to the morphology of the membrane by comparing the fouled membrane with the cleaned membrane, also in comparison to the virgin membrane [16].

Scanning electron microscopy (SEM) analysis was performed to investigate the effect of chemical cleaning on the membrane. The membrane surface was closely analyzed through the images gathered from SEM analysis, which was used as the basis in evaluating the extent of adhesion of foulants on the membrane surface [16–19].

2. Materials and methods

2.1. Membrane and dead-end filtration

Polyvinylidene fluoride (PVDF) hollow fiber membrane was used in this study, which is widely employed in microfiltration and ultrafiltration. Advantages of PVDF membrane include high mechanical strength, high thermal stability, low cost, and high chemical resistance [20,21]. The fouled membrane samples were obtained from a pilot plant treating river water. Specification of the hollow fiber membrane is summarized in Table 1. Dead-end filtration experiment was conducted at constant pressure of 0.5 bar. The initial flux using the virgin membrane was recorded with an average value of 100 LMH. The flux of the fouled membrane was observed to decrease significantly obtaining only 31 LMH.

Table 1
Specification of MF membrane was used in experience

Shape	Hollow fiber module
Pore size, μm	0.038
Material	PVDF
Average filtration flux, L/m^2h	100
Membrane area, m^2	2.26×10^{-3}
Dimension ($\pi \times D \times l \times$ unit)	$\pi \times 150\,mm \times 1.2\,mm \times 4$ units
Operating pressure, bar	0.5

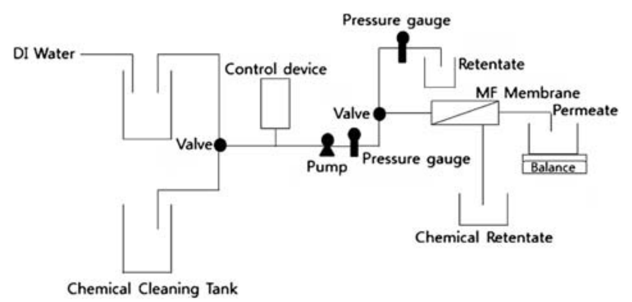

Fig. 1. Configuration of the dead-end filtration system in this experience.

The schematic diagram of the laboratory-scale microfiltration (MF) system is shown in Fig. 1. First, deionized (DI) water flowed into the feed tank. When chemical cleaning started, the valve was closed for the feed tank and the cleaning agent was pumped. The cleaning agent was contained in the chemical cleaning tank. It passed through the valve and its flow was controlled by a gear pump. The pressure was set at 0.5 bar through a pressure gauge.

2.2. Type of chemical agent

Chemical cleaning agents tested in the study were alkaline, organic acid and inorganic acid. For the alkaline, chemical agents used were NaOH and NaOCl. While for inorganic acids, the two cleaning agents were sulfuric acid and nitric acid. And for organic acids, citric acid, and oxalic acid were tested.

2.3. Single chemical cleaning

Chemical cleaning was conducted using NaOH, NaOCl, H_2SO_4, HNO_3, $C_6H_8O_7$, and $C_2H_2O_4$ as cleaning agents and diluted to make different percent concentrations of 0.1, 1, 3, and 5%.

To determine the effectiveness of each chemical for single cleaning on flux recovery, each chemical was passed on the surface the mini-module of the MF system at 30 min contact time and 10 min rinsing with DI water. Thereafter, flux recovery was measured using DI water for 30 min. The experiment was repeated at different contact times 1, 2, and 4 h. The flux was calculated using the equation

$$\text{Flux(LMH)} = \frac{Q}{A} \times \frac{\omega^T}{\omega^{25}} \times \frac{0.5\ \text{bar}}{\text{TMP}} \quad (1)$$

where Q is the filtration flow rate, A is the effective area of the membrane, ω^T is the viscosity at actual temperature, and ω^T is the viscosity at 25℃. The equation used to calculate the recovery rate is as follows:

$$\text{Recovery rate } (\%) = \frac{Flux_A - Flux_F}{Flux_I - Flux_F} \times 100 \quad (2)$$

where $Flux_A$ is the flux after chemical cleaning, $Flux_F$ is the flux of the fouled membrane, and $Flux_I$ is the initial pure water flux.

2.4. Chemical cleaning in series

The chemical cleaning was also conducted by subjecting the fouled membrane with different chemical agents in series. Two sequences were tested, acid–alkaline–acid and alkaline–acid–alkaline.

First, the mini-module was made using the fouled membrane obtained from the pilot plant. Then, the initial flux was measured using DI water. This was followed by chemical cleaning at 1-h duration using either acid or alkaline agent. Second cleaning was conducted with 2-h duration, and the last cleaning with 1 h. Immediately after the chemical cleaning, the flux of the cleaned membrane was measured using DI water, and then, the percent recovery rate was calculated.

The duration of the chemical cleaning was altered from 4-h total cleaning time to 8 h, with cleaning sequence of 2–4–2 h. Through this, the effect of the cleaning agent on the recovery rate can be investigated at two different contact time. Moreover, the effect of temperature on membrane cleaning was also investigated by changing the temperature from 25 to 2℃, and the experiment was carried out with the same procedure [22,23].

3. Results and discussion

3.1. Results of single chemical cleaning

Six chemical cleaning agents were used in this study:

sodium hydroxide (NaOH), sodium hypochlorite (NaOCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), citric acid ($C_6H_8O_7$), and oxalic acid ($C_2H_2O_4$). Each chemical agent was prepared at 0.1, 1, 3, and 5% concentration, and the pH of each solution is listed in the Table. 2. Generally, chemical cleaning operated at pH higher than 12 could damage the PVDF membrane. However, to investigate the effect of pH at harsh conditions, the experiment was still conducted even if the pH of the solution exceeds pH 12.

As shown in Table 3, among the cleaning agents, NaOCl obtained the highest percent recovery rate and flux of 57.7% and 59.6 LMH, respectively, with a cleaning solution concentration of 5% and chemical cleaning time of 4 h. NaOH can also be an alternative based on percent recovery rate and flux of 40.2% and 55.2 LMH, respectively. However, with 3 and 5% NaOH over pH 13, browning of the mini-module was observed due to the partial dissolution of the epoxy on the potting site making it undesirable to use.

Two types of alkaline agents were compared. NaOCl recorded higher recovery rate than NaOH. Membrane fouling was visually observed on the experiment carried out at 5% NaOCl. For NaOH, fouling on the membrane surface was detected with cleaning solution concentration of only 1%. Thus,

Table 2
pH of cleaning solutions at different percent concentrations

Chemical	0.1%	1%	3%	5%
NaOCl	11.10	11.76	12.10	12.23
NaOH	12.82	13.13	13.44	13.89
H_2SO_4	1.72	0.78	0.56	0.34
HNO_3	1.59	0.75	0.34	0.12
$C_6H_8O_7$	2.41	2.24	2.12	1.90
$C_2H_2O_4$	2.29	1.48	1.22	1.08

Table 3
4 hours duration time recovery rate (%)

	NaOH	NaOCl	H_2SO_4	HNO_3	$C_2H_2O_4$	$C_6H_8O_7$
0.1%	14.8	20.6	9.2	9.3	24.5	7.7
1%	23.6	44.0	17.4	10.6	38.1	14.0
3%	20.2	51.5	25.4	27.0	39.1	19.4
5%	40.2	57.7	13.8	37.2	43.4	11.6

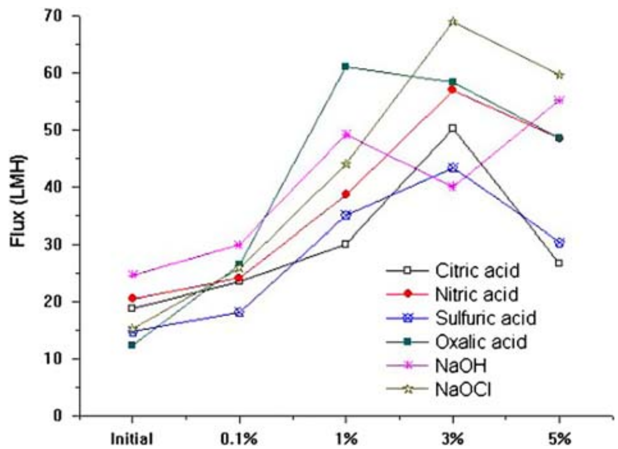

Fig. 2. Flux of single chemical cleaning.

cleaning agents with pH values more than 12 could damage the membrane and increase the tendency of membrane fouling.

For the inorganic cleaning agents, the highest percent recovery rate was obtained using 3% sulfuric acid with 25.4% and flux of 43.4 LMH flux. However, 5% nitric acid showed better performance with 37.2% recovery rate and flux of 48.6 LMH.

As compared to citric acid, the cleaning performance of oxalic acid was much better attaining an average percent recovery rate of 43.4% at 5% concentration. However, among the cleaning agents tested, NaOCl achieved the highest percent recovery rate. This proves that the NOMs from feed water causing membrane fouling could be efficiently removed by NaOCl as a cleaning agent (see Fig. 2).

3.2. Experimental results of the chemical cleaning in series

From the results obtained from single chemical cleaning, the two most efficient cleaning agents, NaOCl and oxalic acid, were chosen for the chemical cleaning in series experiment. The experiment was conducted at constant cleaning solution concentration of 1%, which served only as a basis for comparison, even though the highest percent recovery rates were achieved at 5% concentration. Moreover, 3 and 5% NaOCl exceeded pH 12, which is considered to be harmful for PVDF membranes, and thus, 1% NaOCl was used. For the oxalic acid, purification plants usually employ oxalic acid at a concentration range of 1–3%, and based on the results, the difference between the two percent recovery rates was only 1%, which is very low or incomparable. Therefore, 1% was selected as the standard cleaning solution concentration.

The most efficient cleaning sequence was oxalic acid–NaOCl–oxalic acid at both operating temperatures of 2 and 23˚C with cleaning duration of 2–4–2 h, respectively, as shown in Fig. 3. The highest percent recovery rate was recorded at 64.8% with flux of 73.4 LMH at 23˚C. Operation in series mode was more efficient that single chemical cleaning; however, direct comparison between two modes could not be elucidated due to the difference on the total cleaning time. It should be noted that for a single chemical cleaning, the total cleaning time was 4 h, which is half of the total cleaning time for the operation in series mode. Nevertheless, membrane cleaning in series has higher potential for flux recovery.

Fig. 4 illustrates the percent recovery rates of different cleaning agents as well as their combinations.

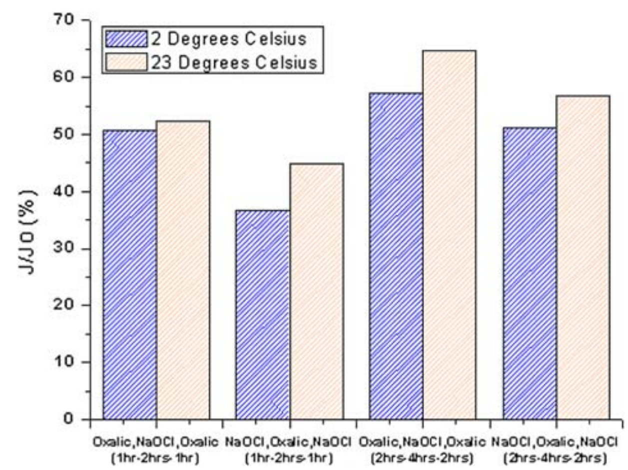

Fig. 3. Recovery rate of chemical cleaning in series at different operating temperatures.

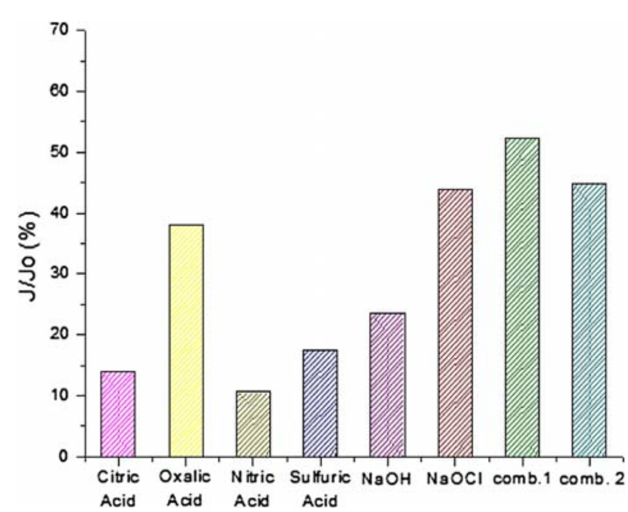

Fig. 4. Recovery rate of various cleaning agents at 1% chemical concentration.

All solutions were tested at 1% concentration to determine the most efficient cleaning agent for chemical cleaning. The results showed that the highest percent recovery rate was achieved using combination 1 (oxalic acid–NaOCl–oxalic acid) attaining 52.3%. Chemical cleaning in series was proven to be very effective in recovering flux, obtaining the two highest recovery rates as shown in Fig. 4, with NaOCl–oxalic acid–NaOCl combination recovery rate of 44.8%.

3.3. Effect of temperature

Chemical cleaning is usually done in elevated temperature to assure high-flux recovery rate. To investigate the effect of temperature on membrane cleaning, the system was operated at lower temperature. Fig. 3 shows the comparison between two different operating temperatures (2 and 23℃). The highest percent recovery rate at 2℃ was achieved by the chemical cleaning sequence of oxalic acid–NaOCl–oxalic acid with 57.2% and duration time of 2–4–2 h. However, cleaning performance was better at 23℃, obtaining percent recovery rate of 64.8%, which is 11.6% higher than the recovery rate at 2℃.

3.4. Membrane morphology by SEM analysis

SEM analysis was conducted after cleaning the fouled membrane. Fig. 5 shows the surface of the membrane at the end of the experiment, and it was observed that the pores of the virgin membrane (Fig. 5) were completely blocked and covered with foulant as shown in Fig. 5. Traces of foulant were still present after cleaning the membrane with 1% NaOCl and oxalic acid. Cleaning sequence of oxalic acid–NaOCl–oxalic acid with total cleaning time of 8 h was found to be more efficient based on percent recovery rate. In addition, combination chemical cleaning was also found an effective means against pore blocking.

3.5. Measurement of tensile strength

Tensile strength was evaluated by analyzing the values of Young's Modulus (MPa) of the virgin membrane, fouled membrane, and cleaned membrane. Stress and strain of the material between the constant of proportionality is called the modulus of elasticity, also called Young's Modulus. Hooke's Law is a direct proportion to the straight gradient expressed as follows:

$$\sigma = \mathrm{E} \times \varepsilon \qquad (3)$$

where σ is the stress, E is Young's Modulus ($E = \tan\theta = \frac{\Delta\sigma}{\Delta\varepsilon}$), and ε represents the strain.

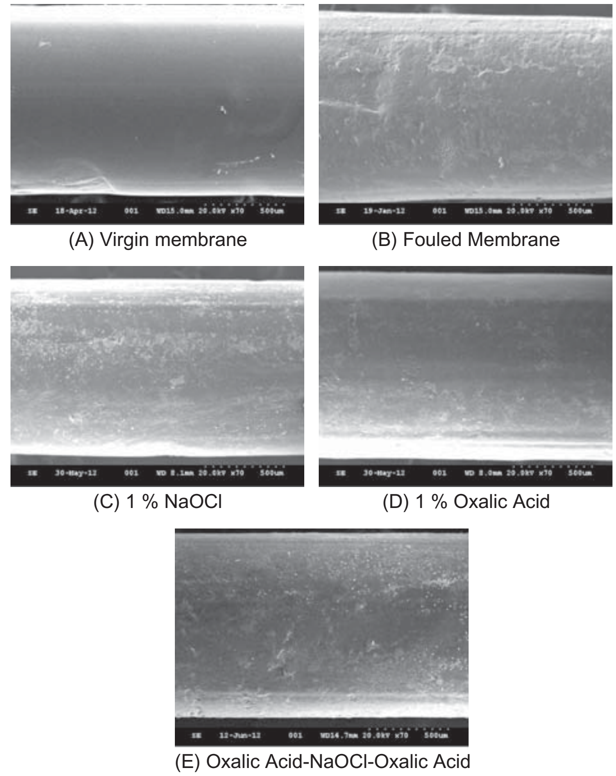

Fig. 5. SEM images of (A) virgin membrane, (B) fouled membrane, (C) after cleaning with 1% NaOCl, (D) after cleaning with 1% oxalic acid, and (E) after cleaning in series with oxalic acid–NaOCl–oxalic acid (2 h-4-2 h).

Young's Modulus is commonly used in the structural material for stress and strain linear relationship. The tensile strength was measured by pulling the hollow fiber strings 10 cm up and down at a rate of 10 mm/min. Three trials were performed, and the values were averaged.

Young's Modulus of the virgin membrane and fouled membrane were 10,160.5 and 3,418.5 MPa, respectively. After conducting the chemical cleaning at 1% concentration, the highest Young's Modulus was recorded using NaOH as the cleaning solution with 9,568.5 MPa, while the lowest was observed using the combination of NaOCl–oxalic acid–NaOCl (1–2–1hr) with 3,142.5 MPa. As shown in Fig. 6, membrane cleaning using a single chemical agent was more efficient than combination of chemical agents. In addition, alkaline agents performed better than organic acid. Citric acid Young's Modulus was higher than Oxalic acid. But Citric acid recovery rate was lower than Oxalic acid. Lower recovery rate chemicals are Young's Modulus is the better than higher recovery rate chemicals.

Thus, if make a combination, should not using organic acid. Because of organic chemicals have a low

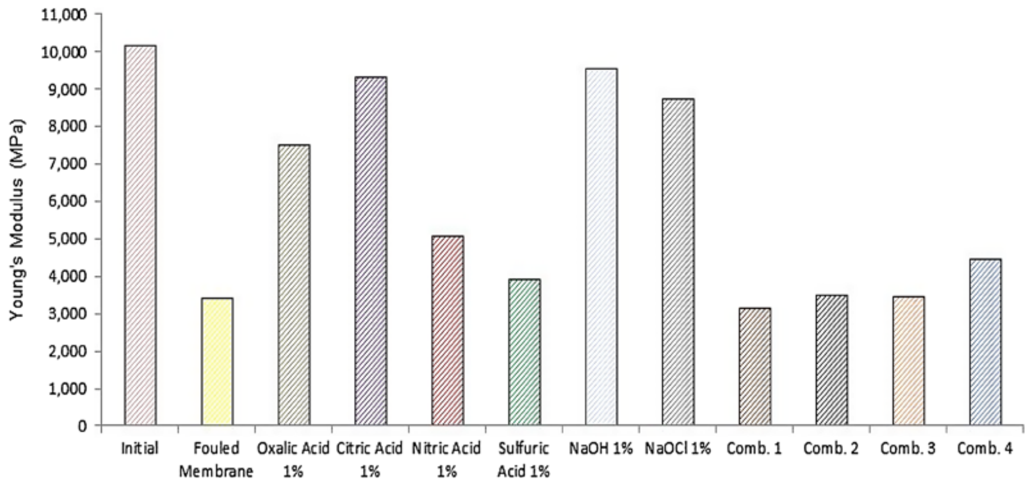

Fig. 6. Young's modulus (MPa) of various cleaning agents.

Young's Modulus and Young's Modulus has in inverse proportion to chemical recovery rate.

4. Conclusions

From the results, it was clear that flux recovery rate was affected by the kind of chemical cleaning agent used.

NaOCl was better than NaOH in cleaning efficiency. Although the recovery rate increase with the concentration 1% would be appropriate in consideration of pH. Because of PVDF membrane could be brittle in the exposure to high pH over 12 for long time. For the acid chemical cleaning agents, 1% oxalic acid was the most effective, with a recovery rate of 38.1%. For combinations of chemical cleaning, Oxalic acid–NaOCl–oxalic acid was observed to be the most effective at 8-h cleaning time, with recovery rate of 64.8%. Cleaning efficiency was directly affected by cleaning temperature. Higher efficiency was achieved at higher cleaning temperature, and lower efficiency was achieved at lower temperature. High tensile strength was observed with low-flux recovery rate in single chemical cleaning and low tensile strength was observed with high-flux recovery rate in combination chemical cleaning.

This experiment was conducted in batch mode, and thus, further research is needed to study the effect of chemical cleaning in a continuous mode.

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