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Effect of a longer cleaning-frequency period on nanofiltration membrane fouling for long-term water supply production

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ABSTRACT

A decline in membrane flux is recognized to occur for a long-term period of system operation and then followed by fouling later. Cleaning of membranes to restore the permeate flux is needed. This research focuses on the effect of a cleaning frequency period on nanofiltration membrane fouling for long-term water supply production. The experiments were conducted in a pilot-scale system, using the treated water after sand filtration from Bangkhen water treatment plant in Bangkok city. Microfiltration process was used as a pre-treatment before nanofiltration process. From the experimental results, it was found that providing a longer cleaning-frequency period of a nanofiltration system tended to decrease in the permeate flux. The flux dropped at around 16, 40, and 71% from the initial stage for each phase of 1, 2, and 3, respectively. Phase 1, 2, and 3 refer to a cleaning frequency period at every 30, 40, and 45% flux drop, respectively. Moreover, for phase 3, it was found that there was no flux recovery at the end of cycle 2, meaning that pore blocking was predominant and the result was confirmed by a pore-blocking mathematical model. In this experiment, the mechanism of fouling started with membrane resistance followed by cake formation, and finally pore blocking mechanism. Furthermore, nanofiltration fouling index (NFI) was developed in this study to indicate a degree of fouling and to prevent irreversible membranes. The NFI less than 0.6 could indicate severe membrane fouling due to pore blocking phenomena. The experiment also suggested that cleaning of nanofiltration membranes should be conducted before 40% of flux decline because the membrane flux could be able to restore with high treatment efficiency.

Keywords: Nanofiltration membrane; Fouling; Nanofiltration fouling index (NFI); Membrane cleaning period; Long-term water supply production

1. Introduction

Nowadays, one of novel technologies to upgrade water quality for drinking purpose is a nanofiltration membrane process. The major problem of the membrane process is fouling phenomenon, which is complicated for understanding. Therefore, control of membrane fouling is very important for nanofiltration technology. In the nanofiltration process, foulant–membrane and foulant–foulant interactions can result in nanofiltration membrane fouling. These interactions are controlled by chemical characteristics of foulants and membranes, solution chemistry, operational environment and permeation drag force. Membrane fouling can be induced and accumulated in many directions. Also, various pollutants in feed water components such as dissolved macromolecu-

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lar organic compounds, soluble inorganic compounds, colloidal and suspended particles and microorganisms can be good examples of these foulants. Several studies have demonstrated that natural organic matter (NOM) and cleaning frequency period play an important role in membrane fouling in water treatment applications [2]. The high molar mass hydrophobic fraction of NOM has generally been found to be responsible for membrane fouling [3–5]. NOM is one of the foulants that reduces membrane performance during filtration in water treatment plants. The optimized cleaning strategies need to operate the membrane testing unit economically and to enhance membrane performance. Lee et al. [6] demonstrated that both cleaning time and cross flow velocity as well as cleaning solution affect cleaning efficiency.

Membrane fouling is a main cause of permeate flux decline through the membrane operation, and also increases flow resistance due to pore blocking, concentration polarization, and cake formation [7]. The characteristics of flux reduction by fouling during membrane operation is shown in Fig. 1. Membrane pore size, solute loading, size distribution, membrane material and operating conditions can be important parameters that affect flux decline in membrane fouling [8,9]. Long-term membrane fouling may lead to irreversible fouling, severe flux decline and reduction of membrane lifetime. Economic viability maintenance of a membrane process is how to minimize membrane fouling as much as possible. Various strategies have to be devised for membrane fouling reduction and improvement of membrane cleaning efficiency for flux recovery [10,11]. These strategies also include a new design of a membrane module [12,13], and incorporation of in situ or ex situ cleaning regimes in a membrane unit [14,15]. Sometimes, a combination of various strategies may be employed in the same process to solve membrane fouling problem [16].

The purpose of this research is to study the effect of cleaning frequency period on nanofiltration membrane fouling for long-term water supply production. The mathematical model of nanofiltration membrane fouling was also investigated. Moreover, the result from this research was used to develop a nanofiltration fouling index that will be used as an indicator in the system operation and information on fouling phenomena for a nanofiltration membrane treatment plant.

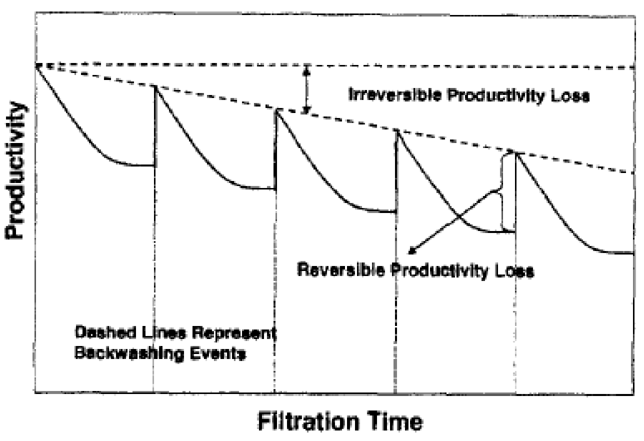

Fig. 1. Typical membrane operation flux decline and cleaning [1].

2. Mathematical models for membrane fouling

The permeation flux of particle-free water across a clean membrane can be described by Darcy's law as:

$$J = \frac{\Delta P}{\mu R_m} \tag{1}$$

where J ($m^3\ m^{-2}\ s^{-1}$) is the permeation flux, ΔP (Pa) the transmembrane pressure (TMP), μ (Pa s) the absolute viscosity of the water, and R_m (m^{-1}) the hydraulic resistance of the clean membrane (or clean membrane resistance).

For suspension filtration, the permeation flux will always be lower than that given by Eq. (1). Flux decline is a result of the increase of membrane resistance to the permeating flow, resulting from membrane fouling or particle deposition on or in the membrane. The mechanisms of membrane fouling usually include pore blocking, concentration polarization and cake formation [3,5,9]. For high molecular weight contaminants, fouling by concentration polarization may be negligible due to the large size of the particles retained [3]. Thus, the permeation flux through a nanofiltration unit treating suspensions can be given, by modifying Eq. (1), as:

$$J = \frac{\Delta P}{\mu\left(R_m + R_p + R_c\right)} \tag{2}$$

where R_p (m^{-1}) is the resistance due to pore blocking, and R_c (m^{-1}) the resistance arising from cake formation. For membrane process at a constant TMP, the initial permeate flux, J_0, will mainly depend on R_m as R_p and R_c are initially zero. With proceeding of the membrane operation, pore blocking and cake formation will cause R_p and R_c to increase, and change the relative significance of R_m, R_p, and R_c in Eq. (2), and the process can transfer from a membrane resistance-limited to a pore blocking resistance-limited or a cake resistance-limited process. According to Wiesner et al. [9], the permeation fluxes under each of theses cases may be given as:

Membrane resistance limited

$$J = \frac{J_0}{\left(1 + J_0 \cdot K_m \cdot t\right)} \tag{3}$$

Cake resistance-limited

$$J^2 = \frac{J_0^2}{\left(1 + J_0^2 \cdot K_C \cdot t\right)} \tag{4}$$

Pore blocking resistance-limited

$$J = J_0 \exp\left(-K_p \cdot t\right) \quad (5)$$

Eqs. (3)–(5) can be rewritten in a linearized form as:

Membrane resistance-limited

$$\frac{1}{J} = \frac{1}{J_0} + K_m \cdot t \quad (6)$$

Cake resistance-limited

$$\frac{1}{J^2} = \frac{1}{J_0^2} + K_c \cdot t \quad (7)$$

Pore blocking resistance-limited

$$\ln(J) = -K_p \cdot t + \ln(J_0) \quad (8)$$

where K_m, K_c, and K_p are system constant parameters relating to membrane resistance, pore blocking resistance, and cake formation resistance, respectively.

3. Experimental methods

The experiment was conducted in a pilot-scale system at Bangkhean Water Treatment Plant, Bangkok, Thailand. In this study, treated water from the sand filter at the water treatment plant was fed into the NF process, using a microfiltration membrane as pre-treatment and followed by a nanofiltration membrane. Here, the microfiltration membrane was a hollow fiber module with a surface area of 8 m^2 manufactured by Mitsubishi Rayon, Japan. The nanofiltration membrane used in this experiment was ESNA1-4040 that has ability of 85% NaCl rejection at 5 bar. It is made from composite polyamide, and manufactured by Nito Denko Co., Ltd. The chemicals used for nanofiltration membrane cleaning were EDTA and citric acid. The experimental set-up system is shown in Fig. 2.

All experiments were operated in continuous mode of operation. The long-run operation of the NF process for water supply production has 3 phases in order to investigate different membrane cleaning frequency periods as described below. Each phase was conducted with 3 consecutive operating cycles.

- Phase 1: The cleaning frequency period was performed every flux decline 30% from the initial stage of each cycle.
- Phase 2: The cleaning frequency was performed every flux decline 40% from the initial stage of each cycle.
- Phase 3: The cleaning frequency was performed every flux decline 45% from the initial stage of each cycle.

The result from the experiment will be used to describe fouling phenomena of the nanofiltration membrane and also to develop the nanofiltration fouling index in order to indicate fouling phenomena of this process.

4. Results and discussion

4.1. Effect of a longer cleaning frequency period on pollutant removal

The effect of the cleaning frequency period on pollutant removal was investigated in this study as shown in Table 1. The experimental data showed that an increase of longer cleaning frequency had an insignificant impact on water quality in terms of hardness, NOM as UV_{254}, turbidity, conductivity, TOC, and some ions in water. From the NF system operation, the results of various anion removals show that anion with more negative charge such as sulfate ion had a higher potential for removal efficiency. These removal phenomena can depend on surface charge and size of anions in the solution and also membrane surface charge. The effect of ion charge is confirmed by the results of SO_4^{2-} and NO_3^- removal efficiencies. SO_4^{2-} had higher removal efficiency than that of NO_3^- because SO_4^{2-} has higher negative charge than that of NO_3^-, so the repulsion force can be higher. The effect of lyotropic series (increasing rejection with increasing hydrated radius) is also confirmed by the results of NO_3^- and Cl^- removal efficiencies. In this study the removal efficiency of Cl^- was higher than that of NO_3^- because Cl^- has higher hydrated radius than NO_3^-, as a result the rejection force was also

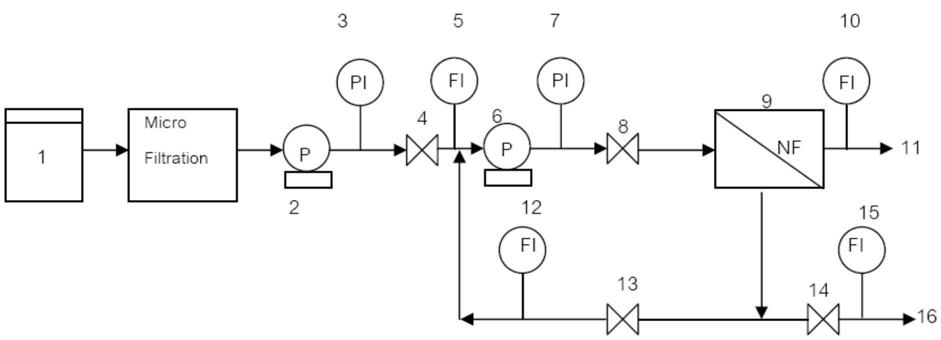

Fig. 2. Schematic diagram of the experimental set-up system for the NF process. 1 – Influent storage; 2,6 – Pump; 3,7 – Pressure gauge; 4,8,13,14 – Ball valve; 9 – Nanofiltration module; 5,10,12,15 – Flow meter; 11 – Permeate; 16 – Concentrate.

Table 1
Effect of cleaning frequency period on pollutant removal percentage

Parameter	Pollutant removal percentage (%) at each membrane cleaning frequency period		
	Every 30% flux drop	Every 40 % flux drop	Every 45 % flux drop
Conductivity	90.26±1.26	90.27±0.73	90.00±1.14
Turbidity	100.00±0.00	100±0.00	100±0.00
NOM as UV_{254}	93.23±4.18	91.12±4.56	90.70±4.16
Total hardness	91.82±3.01	90.80±2.18	92.46±2.10
Ca^{2+} hardness	90.77±3.94	91.11±3.22	93.06±2.10
Mg^{2+} hardness	92.37±9.15	89.00±8.28	91.44±3.48
TOC	99.00±0.70	95.47±3.15	95.59±1.79
F^-	100.00±0.00	99.19±2.43	98.59±0.99
Cl^-	91.60±1.70	90.78±1.68	89.69±1.28
NO_3^-	78.56±3.24	75.44±3.99	75.61±4.99
SO_4^{2-}	99.97±0.16	99.97±0.14	99.98±0.01
THMFP	52.23±4.30	50.99±3.87	51.16±3.90

higher due to sieving mechanism. It can be concludeed that although the nanofiltration membrane had a great efficiency in water quality improvement for water supply production, the longer cleaning frequency period seemed to insignificantly improve water quality of the membrane permeate.

4.2. *Effect of a longer cleaning frequency period on fouling mechanism*

The experimental data showed that the longer cleaning frequency period expanded from every 30–40 and to 45% flux drop, had affected on the permeate flux and fouling mechanism that are shown in Figs. 3 and 4. The result from Fig. 3 shows that providing a longer cleaning-frequency period of the nanofiltration system tended to decrease in the permeate flux. The flux dropped at around 16, 40, and 71% from the initial stage for each phase of 1, 2, and 3, respectively. Phase 1, 2, and 3 refer to cleaning frequency period at every 30, 40, and 45% flux drop, respectively. The data of flux recovery percentage, compared to the initial stage of operating cycle for each phase of the cleaning period are shown in Fig. 4. The results show that when the operation cycle was increased, the membrane cleaning at every flux reduction as 30 and 40% from initial stage still could obtain better percentage of flux recovery after cleaning. Moreover, the membrane cleaning at every 45% flux decline could not recover the flux performance when operating to cycle 3 in phase 3, it can refer that the system was critical in this operation. The result showed that cleaning membrane at every flux drop as 30 and 40% from the initial stage could be related to the fouling mechanism by predominant cake formation that was confirmed by cake formation linearized graphic curve fitting in Figs. 5a and 5b. In the cake formation phenomena the membrane flux decreased, which might be caused by surface foulants, but it could restore the efficiency back by membrane cleaning. In the membrane cleaning every flux decline at 45% from the initial stage, no flux recovery was found at the end of cycle 2, meaning that pore blocking was predominant and the result was confirmed by pore blocking linearized graphic curve

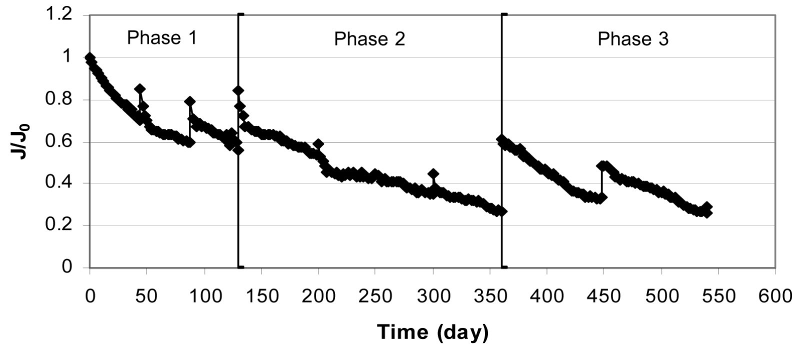

Fig. 3. Flux decline from the initial stage due to operation time (Phase 1, 2, 3: Cleaning period at every 30, 40, 45% flux drop, respectively).

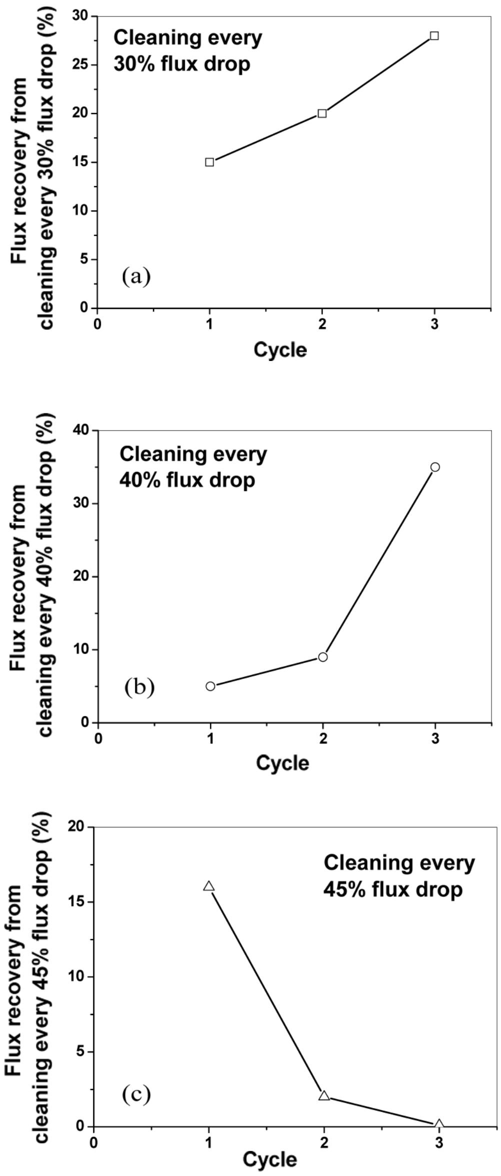

Fig. 4. Percent of flux recovery at every cleaning frequency period at 30% (a), 40% (b), and 45% (c) flux drop from the initial stage.

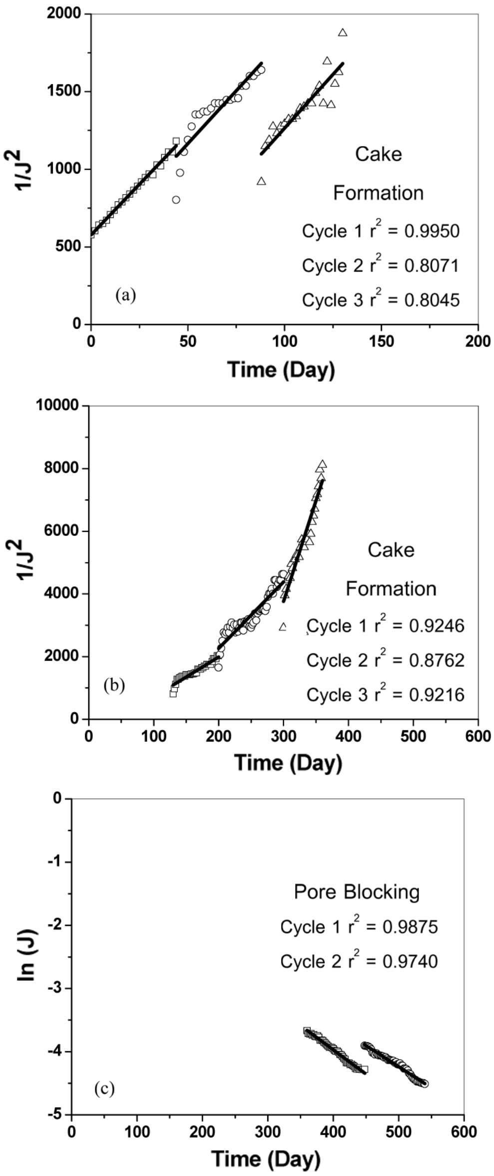

Fig. 5. Linear graphic curve fitting for the system with cleaning every 30% (a), 40% (b), and 45% (c) flux drop from the initial stage.

fitting in Fig. 5c. The mechanism of pore blocking mainly occurred in the condition of membrane fouling at the end of the operation.

4.3. *Fouling mechanism and nanofiltration fouling index development*

The flux decline of the membrane system can indicate fouling mechanism. The result of fouling in terms of fouling line is shown in Fig. 6. The data from Fig. 5 (mathematical model prediction) and Fig. 6 (flux recovery line) can indicate the predominant fouling mechanisms, generated in phase 1, 2, and 3, there might be predominant cake formation in phase 1 and 2, and significant pore blocking in phase 3, respectively. It is also observed from Fig. 6 that the value of relative flux reduction or flux decline line in the last phase was 0.6 which can be used as a fouling index to indicate the significant membrane fouling in order to prevent nanofiltration membrane fouling. It can be concluded that fouling in type of cake formation mechanism was predominant in conditions of relative flux reduction value above 0.6, compared to the initial stage, after that the mechanism could be shifted to predominant pore blocking mechanism at the point of

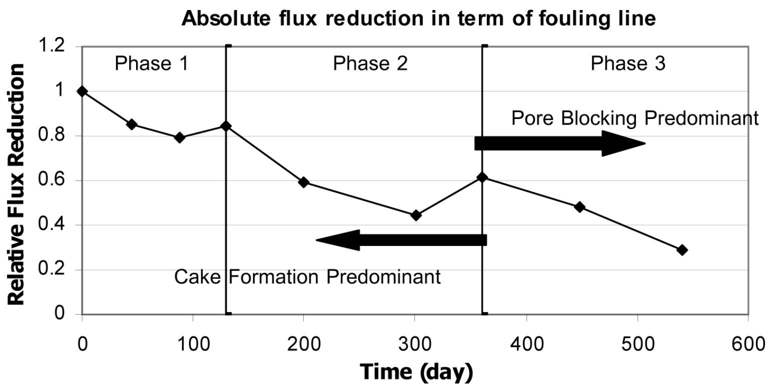

Fig. 6. Absolute flux decline in terms of fouling line for long term water supply production using the nanofiltration membrane (Phase 1, 2, 3: Cleaning at every 30, 40, 45% flux drop, respectively).

relative flux reduction value or fouling index value less than 0.6. Then, the flux recovery could not be obtained, finally. Therefore, the fouling index of the nanofiltration membrane, so called NFI is proposed here to be used as an indicator to identify the degree of fouling to prevent membrane pore blocking for long-term water supply production. The NFI equation is shown in Eq. (9).

Nanofiltration fouling index:

$$\mathrm{NFI} = \frac{J_i}{J_0} \tag{9}$$

where NFI is fouling index of the nanofiltration membrane for long-term water supply production which ranged from 0 to 1. The cake formation mechanism might be predominant at NFI more than about 0.6 and pore blocking mechanism might significantly influence membrane fouling when NFI less than 0.6. J_i is flux after cleaning at time i; J_o is initial flux of nanofiltration membrane at each cycle of operation.

5. Conclusions

1. Longer cleaning frequency period of the nanofiltration membrane has an insignificant impact on water quality removal efficiency but it can result in a degree of fouling level. The dominant fouling mechanisms of cake formation and pore blocking have to be carefully considered to prevent nanofiltration membrane fouling.

2. Fouling index of the nanofiltration membrane for long-term water supply production can be developed from data results in this experiment as shown in the proposed Eq. (9) as NFI = J_i/J_0.

3. Cleaning of the nanofiltration membrane in this water production process should be conducted at relative flux decline above 0.6 in order to prevent irreversible fouling of the membrane due to pore blocking phenomena.

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