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Effect of chemical cleaning on membrane biofouling in seawater reverse osmosis processes

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ABSTRACT

Reverse osmosis (RO) membranes are widely used for desalination plant. However, membrane biofouling cause decreasing membrane performance. This work focused on finding optimum cleaning conditions in RO membrane processes. The effect of cleaning conditions such as agent concentration, temperature and cleaning time on cleaning efficiency were investigated in Centers for Disease Control (CDC) annular biofilm reactor. Alkaline cleaning agent, sodium hydroxide (NaOH) which is well known for removing organic foulant on membrane, was used. Total bacteria number was measured with diamidino-2-phenylindole (DAPI) dye and cell viability were analyzed by using two different DNA-binding dyes (SYTO9/PI). The optimum temperature, cleaning time and cleaning agent concentration were found as 30°C, 20 min and 1.0 wt%, respectively.

Keywords: Desalination; Reverse osmosis membrane; Membrane biofouling; Membrane cleaning; Alkaline cleaning

1. Introduction

Membrane application in water treatment processes including desalination and wastewater treatment has been recognized as a promising technology to increase water supply. However, membrane fouling has been a severe problem because it significantly reduces membrane performance efficiency [1]. It causes membrane flux decline, differential pressure and feed pressure increase, membrane biodegradation, salt passage increase, and energy requirements increase [2]. Typically, there are four types of fouling on membrane: inorganic fouling/scaling, particle/colloids fouling, biological fouling and organic fouling [3]. Among these fouling types, biological fouling has been considered as a critical problem due to the formation of biofilms on membrane.

In order to minimize the effect of biofouling, feed water pretreatment and cleaning of membrane processes have been employed. However, biofouling still occurs after the use of pretreatment systems like addition of disinfectants such as chlorine [4]. It was also reported that even though membrane surfaces were exposed to oxidizing agents, bacteria rapidly re-attached and formed biofilms [1]. Therefore, it is important to find effective cleaning process to maintain membrane flux rate and quality.

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Many studies have been studied for searching effective chemical cleaning conditions [1,3,5–7]. However, a few studies worked about the impact of cleaning on cell viability [1]. It was reported that cleaning efficiency depends on cleaning agent, concentration, pH, temperature and cleaning time [6,7]. Among these conditions, cleaning agent can be selected depending on cleaning target. In particular, alkaline agent has been reported that it could be used for dissolution of organic matter from membrane [3,7]. Therefore, the objective of this study was to find biofilm cleaning conditions using sodium hydroxide (NaOH) by measurement of total cell and cell viability in each condition. *Pseudomonas* sp. [4] was used to demonstrate the impact of cleaning agent composition and frequency on biofilm formation under RO process conditions.

2. Methods and materials

2.1. Preparation of sterile synthetic seawater and Pseudomonas sp. strain

The seawater was made by melting sea salt reagent (Sigma-Aldrich, Inc., USA) in deionized water. Total dissolved solid (TDS) value was adjusted to 35,000 mg/L and pH was 8.0. Single strain of *Pseudomonas* sp. P60 which isolated from seawater was grown in Luria-Bertani (LB) broth (BD, USA) at 37°C for 24 h. These bacterial cells were then harvested by centrifugation at 10,000 rpm for 10 min, and washed two times with sterile synthetic seawater and suspended in a volume of sterile synthetic seawater to achieve optical density of 1.0.

2.2. Formation of biofilm on RO membrane

Centers for Disease Control (CDC) annular biofilm reactor (Biosurface Technologies Corp., USA) was used to grow biofilms on the membranes. It consists of eight polypropylene coupon holders having 3 coupons (12.7 mm in diameter). A commercial thin film composite RO membrane, RE8040-SHN (Woongjin Chemical Co. Ltd., Korea), was used as a model membrane for the biofilm experiments. RE8040-SHN membrane is a spiral wound type membrane comprised of polyamide. RO membranes with 1 cm^2 size were attached to polypropylene coupons and soaked into prepared 500 mL synthetic seawater in the 1 L CDC annular biofilm reactor. 5 mL cultured cell having optical density 1.0 were inoculated to reactor. For providing nutrient, 0.1% LB broth (BD, USA) was inoculated in the reactor. All experiments were performed at 28°C under constant rotation at 130 rpm. After 96 h that time reached on stationary phase, RO membranes were detached from coupons.

2.3. Optimization of chemical cleaning conditions

To investigate the effect of chemical agent concentration on membrane biofouling removal efficiency, experimented with variable NaOH concentrations 0.1, 0.5, 1.0, 2.0, 3.0 wt%. Cleaning was performed during 10 min in each 1 ml various NaOH solution. The effect of cleaning time on membrane cleaning efficiency, time conditions were established 5, 10, 15 and 20 min. NaOH concentration and temperature was 1.0 wt% and 28°C, respectively. To study on cleaning temperature effect, experiment performed at different temperature, 20, 25, 30 and 35°C. Because 45°C is a maximum operating temperature of RE8040-SHN RO membrane, above 35°C could not be established. NaOH concentration was 1.0 wt% and cleaning time was 10 min. After cleaning, membranes were rinsed with distilled water and soak into sterilized distilled water. To detach bacteria from the RO membrane, sonication was performed for 5 min by using sonicator (Fisher scientific Inc., USA). Membranes were discarded from the distilled water and analyzed cell number and cell viability. Cleaning efficiency is defined according to Eq. (1):

$$\text{Cleaning efficiency (\%)} = \frac{\text{Total cell number after cleaning process}}{\text{Total cell number of control}} \times 100 \quad (1)$$

2.4. Visualization of biofouled membrane

To verify cleaning effect, based on optimum conditions, the surfaces of the membranes were observed by a scanning electron microscopy (SEM) (S-4700, Hitachi, Japan). Before SEM observation, membranes were pretreated by modified method of reference [4]: The membrane samples were fixed with 4% glutaraldehyde solution (Fluka, Sigma-Aldrich) for 1 h at 4°C then dried subsequently for 5 min at 35°C, and dehydrated for 3 min in each 50%, 80% and 94% ethanol solution. After placing the membrane samples in drying chamber overnight, they were coated with Pt for 35 s by ion sputter (E-1030, Hitachi, Japan) for SEM observation.

2.5. Measurement of cell number and cell viability

Chemical cleaning efficiency was evaluated by means of the measurement of total cell number and cell viability. 4′,6-diamidino-2-phenylindole (DAPI) staining was used to enumerate total bacteria number in the samples. A LIVE/DEAD BacLight staining kit (L-7012, Molecular Probes, USA) was used to enumerate the live and dead bacteria in the samples. Mixtures in the ratio 2:1 of SYTO9 green fluorescent nucleic acid stain and red fluorescent stain, propidium iodide [1] were added to 1 mL of the bacterial cell suspension. Application of these two dyes resulted in the green fluorescence for viable cells and the red fluorescence for dead cells. After staining, fluorescent image was captured by a LSM5 (Zeiss, Germany) inverted confocal laser scanning microscopy (CLSM) equipped with a PC with the LSM software (PASCAL) for control of

all the system components. Imaging was achieved using a C-Apochromat 40× objective. Quantitative analysis of fluorescent signal on image captured from LSM confocal microscope was conducted by the image analyzer software (isolution/Lite, iMTechnology, Korea).

3. Results and discussion

3.1. Effect of cleaning agent concentration

Cleaning efficiency of all experiments was obtained from measuring total cell number and live and dead cell proportions. Cleaning process resulted in reduction of viable bacteria number [8]. The concentration effect on the cleaning efficiency was investigated at various cleaning chemical concentrations.

Fig. 1 shows the impact of NaOH concentrations on cleaning efficiency. At 0.1 wt% NaOH concentrations, it showed the highest value of cleaning efficiency (96.1±1.3%) (Fig. 1a). Although applying high cleaning agent concentration, total cell number was increased in accordance with increasing NaOH concentration. The reason why increasing of total cell number might be hydrophilicity increase on membranes according to pH change (from 13.0 to 14.1). Sohrabi et al. [3] showed increase of hydrophilicity of membrane occurred as pH increases. Increased hydrophilicity could effects on cell attachment on membranes. Even though 0.1 wt% NaOH concentration has high cleaning efficiency, percentage of live cell is higher than other concentration conditions (Fig. 1b). Since *Pseudomonas* has been considered as a fast adhering species [9], untreated live cells cause biofilm re-formation by accelerating re-deposition and re-growth [1]. Therefore, 1.0 wt% NaOH concentration would be optimum concentration rather than 0.1 wt% NaOH for membrane cleaning.

3.2. Effect of cleaning time on cleaning efficiency

To investigate cleaning time effect, cleanings were performed during 5, 10, 15, 20 min. 1.0 wt% NaOH was used as a cleaning agent and maintained temperature at 28°C during experiment (Fig. 2).

Fig. 2a shows similar cleaning efficiency above 10 min cleaning time. However, live cell percent in 20 min cleaning time condition was lower than other conditions (1.7%) (Fig. 2b). Therefore, 20 min result in optimum cleaning duration condition. Blanpain-Avet et al. [10] reported 20 min cleaning time was optimum condition for removing proteins from microfiltration membrane. However, another research presented 60 min cleaning time with NaOH (pH 11) could not attribute to enhance organic fouling removal [11]. Even though long time cleaning is more efficient, above 20 min cleaning duration condition showed biofouling re-formation phenomenon [10].

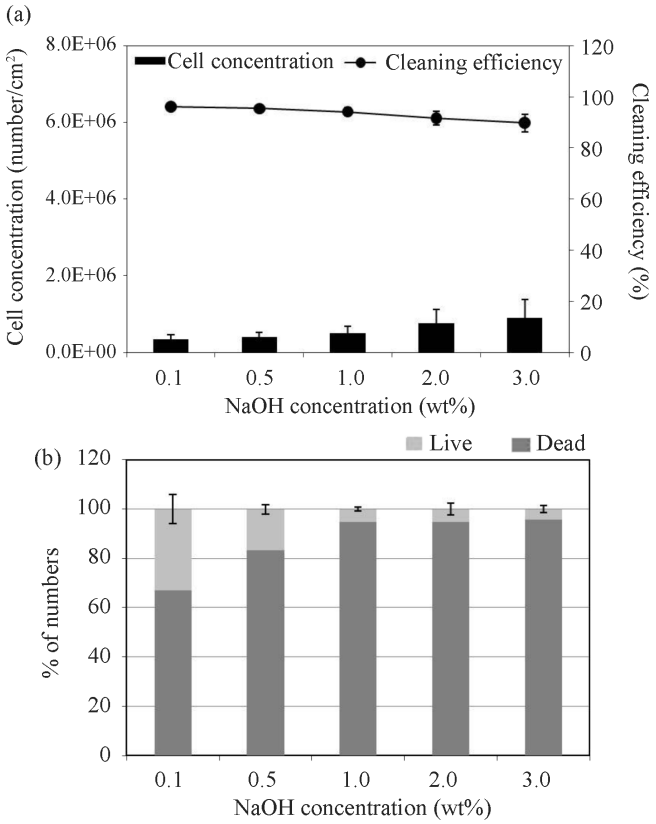


Fig. 1. Influence of various NaOH concentrations on (a) cleaning efficiency and total cell number and (b) cell viability after 10 min cleaning.

3.3. Influence of temperature on cleaning efficiency

To study for influence of cleaning agent temperature on cleaning efficiency and cell viability, cleaning was performed at different temperature conditions. As it can be seen in Fig. 3, bacteria removal efficiency was increased in accordance with increasing temperature from 20°C to 30°C and maintained at 35°C (Fig. 3a). It was reported that high cleaning efficiency at high temperature resulted from decreasing of membrane stability and viscosity of the cleaning solution [3]. Some studies presented high temperature (35–40°C) were optimum condition [3,11,12] (Table 1). However, high temperature is not suitable for practical process due to the restrains of the operational system [13].

Furthermore, similar results in cleaning efficiency and cell viability (Fig. 3b) were achieved both temperature conditions 30°C and 35°C. Therefore, from the viewpoint of economical aspect, cleaning temperature 30°C can be considered as an optimum temperature condition.

3.4. Visualization of biofouled membrane

SEM analysis was used to confirm cleaning effect on RO membranes. Fig. 4 shows the SEM images of fouled

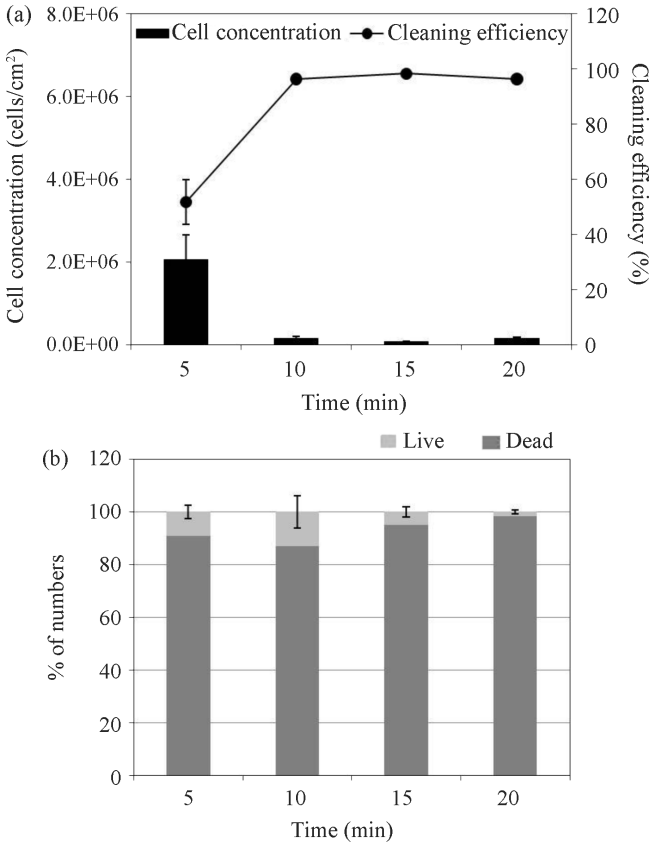


Fig. 2. Influence of cleaning time on (a) cleaning efficiency and total cell number and (b) cell viability by using 1.0 wt% NaOH cleaning solution.

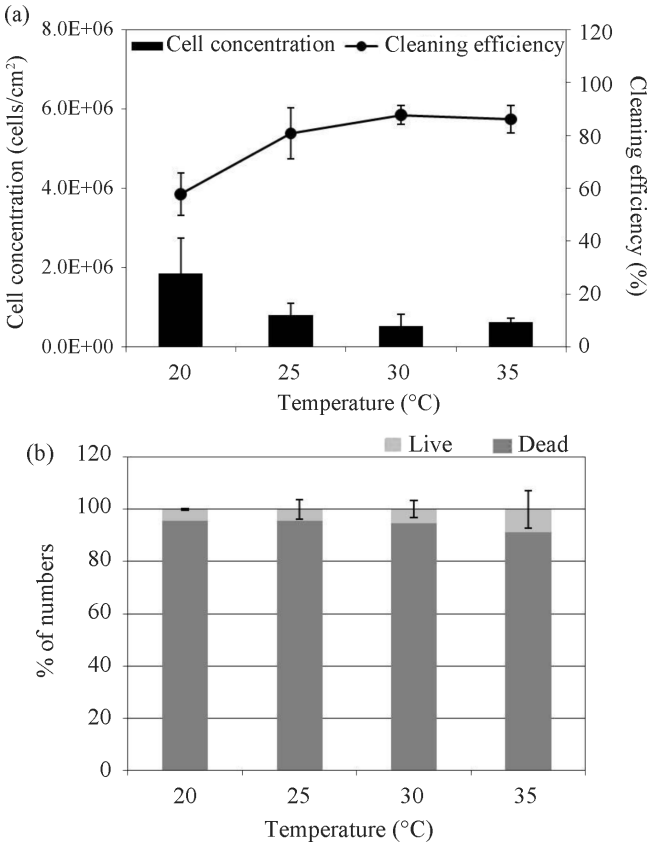
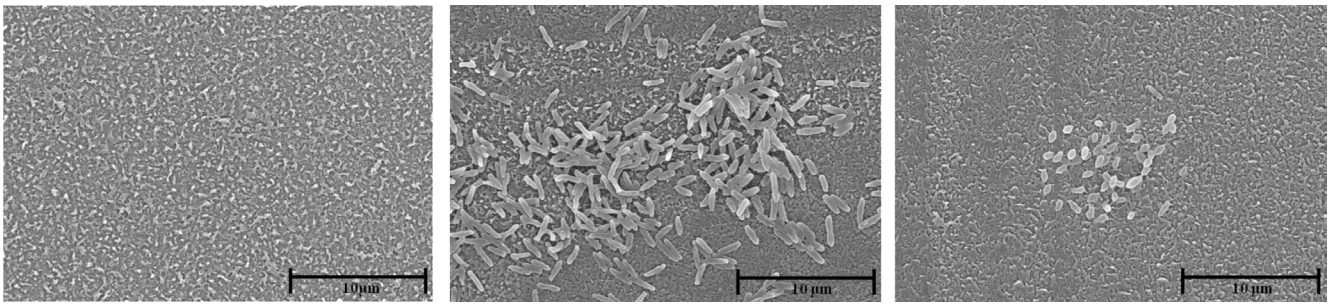


Fig. 3. Influence of cleaning temperature on (a) cleaning efficiency and total cell number and (b) cell viability. Other conditions were 1.0 wt% NaOH concentration and 10 min cleaning time.



(a) (b) (c)

Fig. 4. SEM images of the surface morphologies of RO membranes: (a) virgin RO membrane, (b) fouled RO membrane, (c) cleaned RO membrane (4,000×, S-4700, Hitachi, Japan).

and cleaned RO membranes. Figs. 4a, 4b, 4c indicate virgin, fouled and cleaned membrane, respectively. Comparison cleaned membrane with virgin and fouled membranes confirmed that foulants on membrane were removed effectively. Remained cells can be seen in Fig. 4 were considered due to their strong adhesion on membrane.

4. Conclusions

Biofouling control is important to reduce cost and energy for desalination process. Chemical cleaning is an imperative tool to control biofouling. Cleaning efficiency was determined by flux recovery rate in most of chemical cleaning research. However, due to biofouling

Table 1
Study of chemical cleaning effect on membranes

Cleaning target	Cleaning agent	Membrane	Membrane size	Method	Cleaning efficiency	Reference
Organic fouling	0.1 M NaOH	UF	60 cm^2	24 h cleaning	Flux recovery 64.8%	[14]
	0.1 wt% NaOH	RO, NF	0.002 m^2	Optimum temperature (35°C), cleaning time (20 min), pH (12),	Flux recovery near 100%	[3]
	100 mM $NaNO_3$	RO	N.A.	15 min, 20°C	Flux recovery 89.4%	[12]
	2 mM EDTA	RO	20.0 cm^2	flow	Flux recovery near 100%	[11]
Inorganic fouling	10% ethyleneglycol monobutyrate (EGMB)	RO	63.6 cm^2	6 h	Flux recovery 200%	[15]
Organic/ inorganic fouling	0.1% $Na_5P_3O_{10}$ and 0.2% Na_4EDTA	NF	4 × 7.7 m^2	10 min at low flow rate, 15 min at high flow rate	Flux recovery 106%	[16]
	Distilled water, 0.1 N sulfuric acid, 0.1 N sodium hydroxide	RO	2.1 m^2	Flow	Dissolved inorganic matter removal efficiency 95.3%, Dissolved organic matter removal efficiency about 80%	[17]
	1 M NaOH + 0.05% NaOCl , 1 M HNO_3	MF	N.A.*	Alkali treatment – acid treatment	Flux recovery 76.8%	[18]
Biofouling	0.1 mg/l NaOCl	RO, NF	N.A.	30 min	NaOCl is the best	[1]
	1.0 wt% NaOH	RO	1.0 cm^2	Optimum temperature (30°C), cleaning time (20 min)	Cleaning efficiency 95.2±0.9%	This study

*N.A.: not available

re-formation on the surface of membrane, measurement of total cell number and live and dead cell ratio were needed. This research presented optimum cleaning conditions on RO membranes based on biological cell measurement in CDC annular biofilm reactor. In addition, SEM images showed that biofoulants were successfully removed in optimum cleaning conditions. So far, many studies were performed to find out optimum chemical agent and conditions. However, it is difficult to apply optimum cleaning conditions for reducing biofouling in the field because experimental conditions and size were totally different. Further research is required to establish systematic cleaning conditions.

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