Direct observations of membrane scale in membrane bioreactor for wastewater treatment application

J. Kim and T. I. Yoon

ABSTRACT

The formation of inorganic fouling on MF membrane was investigated in membrane bioreactor (MBR) treating industrial wastewater. Membrane autopsy works using microscopic techniques and surface analysis were carried out at the completion of pilot-scale operation to analyze foulant materials extensively. Scaling occurred on the membrane surface significantly in the MBR treating calcium-rich wastewater (LSI > 2.0). Our experiments showed that the coverage of the membrane surface by the inorganic fouling consisted mostly of calcium while the internal fouling within membrane pores due to the scale formation was almost negligible. Most of calcium was rejected on the MF membrane surface as scale formation of calcium carbonate (>90% as rejection). The sequence sodium hypochlorite-citric acid for the removal of membrane scale was more effective than the sequence citric acid-sodium hypochlorite cleaning. It appeared that the structure of organic compounds combined with calcium became loose by the addition of the sodium hypochlorite, thereby releasing calcium more easily from the membrane by applying the acid cleaning agent.

Key words | calcium carbonate, membrane autopsy, membrane bioreactor, scaling

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INTRODUCTION

Recently, there has been an upsurge of interest in membrane bioreactor (MBR) technology for wastewater treatment. The submerged membrane design is used generally in activated sludge systems with low-pressure driven membranes such as microfiltration (MF) and ultra-filtration (UF) membranes, and does not include a shell to encase the membranes. The MBR technology not only eliminates the need for secondary clarifiers but also produces an effluent quality that exceeds conventional granular media filtration (DiGiano *et al.* 2004).

Although the MBR technologies have many advantages over conventional wastewater treatment technologies, the ability of a membrane to reject contaminants inevitably causes membrane fouling. Fouling results in loss of perfor-mance of the membrane due to the deposition of rejected wastewater constituents on its external surface, at its pore openings, and within its pores (Ho & Zydney 2000;

Germain *et al.* 2005). Many studies on the foulant materials of interest in the aerobic MBR technology for wastewater treatments have focused on the macromolecular organics such as polysaccharides (Chu & Li 2005). Polysaccharides most likely originate from bacterial cell components during biological processing. Bacterial cell components are often referred to as biopolymers or extracelluar polymeric substances (EPS) that could vary widely in wastewater (Jarusutthirak *et al.* 2001).

Inorganic fouling has been recognized as a major problem in aerobic MBRs (Arabi & Nakhla 2008) while efforts to identify inorganic fouling are still lacking as it compares with the organic fouling. The concentration of dissolved inorganic solutes increases in the direction of flow because the volume is reduced as the permeate passes through the membrane. Depending upon the inorganic species and pH, the concentration of one or more solutes

may exceed its solubility product and begin to form a precipitate that causes membrane fouling (Yoon *et al.* 1998). In the membrane coupled with anaerobic bioreactor, inorganic precipitation (e.g. struvite) was responsible for hardening the cake layer at the membrane surface (Choo & Lee 1996). Because the anaerobic MBR is typically enclosed, thus CO_2 partial pressure in the gaseous space of the tank increases and crystallization of calcium carbonate may occur on the membrane surface (You *et al.* 2006). In spite of the number of studies on the anaerobic MBR, however, relatively little effort has been made to perform direct observations of inorganic fouling in the aerobic MBR. In addition, previous studies still fall short of providing real evidence on the inorganic fouling in the aerobic MBR in practice because most studies were based on the bench-scale module treating synthetic wastewater. The objective of this study was to observe inorganic fouling in the pilot-scale testing of aerobic MBR treating industrial wastewater which is characterized as calcium-rich wastewater. Direct examinations by applying microscopic and surface analysis techniques were performed for the extensive analysis of inorganic fouling at the completion of pilot-scale operation in the submerged, aerobic MBR.

METHODS

Pilot-scale operation of submerged, aerobic MBR

The membrane bioreactor (MBR) was installed as pilot-scale and operated to treat wastewater discharged from textile industry. The industrial wastewater from the plant (Kwangjoo, Korea) was pumped into activated sludge at a rate of $30 \, m^3$/day. The pH of the feed wastewater ranged from 7 to 8. The average solid retention time (SRT) was 7 days and hydraulic retention time (HRT) was 10 h. The mixed liquor suspended solids (MLSS) concentration in the reactor was about 3 g/L. The temperature of the mixed liquor varied within the range of 20 and 25°C. The MBR system consisted of an activated sludge bioreactor and hollow-fiber MF membrane modules submerged into the reactor. Modules were directly installed into the aeration tank with horizontal configuration and aeration pipe with 6 mm hole was equipped below the module to generate coarse bubbles on the membrane

surface. Aeration was provided at the bottom of the reactor with $0.75 \, Nm^3/m^2$/min as air flow rate. Filtration was performed under constant flux of about $17 \, L/m^2$/h with suction pump controlled automatically.

Membranes

The submerged, hollow-fiber membrane module was manufactured from KOLON industries Inc., and applied for the pilot-scale operation. The hollow-fiber membrane was fabricated from polyvinylidenefluoride (PVDF) materials with braid reinforcement to improve system integrity by preventing its damage possibly caused by the sway of hollow fibers in the bioreactor. The reinforced hollow-fiber membranes have shown ideal performance in the application of the MBR system in terms of filterability and mechanical properties attributed to the thin layer of PVDF membrane and braid reinforcement, respectively. The nominal pore size of the membrane was $0.1 \, \mu m$. The hollow fiber membrane has an inner diameter of 0.8 mm, outer diameter of 2.0 mm and length of 1 m.

Measurement of inorganic fractions in foulant materials

Membrane autopsies were performed to investigate scale formation on the membrane surface at the end of pilot-scale operation of aerobic MBR. At the completion of the MBR operation, a coupon of hollow-fiber membrane was placed on a sample mount and examined in the scanning electron microscope (SEM). The SEM (Model: Hitachi S430) was applied with an accelerating voltage of 5 kV and a working distance of about 13.2–16.0 mm depending upon magnification. The magnification of about $50–120 \times$ was applied to obtain the appropriate resolution of the samples. The membrane sample cut from the fouled membrane was mounted with double-side tape on aluminum stubs, and sputter coated with a thin layer of conductive metal (Au). Secondary electron (SE) images were also taken at high magnification ($120 \times$). The targeted energy dispersive X-ray analysis (T-EDXA Model: Noran EDX System) uses the SE image to determine the inorganic elemental composition of the foulant materials. The wavelength of the X-rays produced was used to identify the presence and relative

amounts of the chemical elements in the foulant material. A small portion of foulant material was placed in KBr pellets for Fourier Transform Infrared analysis (FTIR). This was followed by spectral interpretation obtained from reflection mode and a library search of inorganic chemicals. The FTIR spectrum (The Nicolet/Thermo Electron Avatar 360) was obtained with virgin membrane for the reference to compare with chemically cleaned membrane. Inductively coupled plasma mass spectroscopy (ICP-MS) was also applied for analyzing trace elements in the feed wastewater and cleaning solutions tested in this study.

RESULTS AND DISCUSSION

Characteristics of feed wastewater

Result of inorganic constituents in textile feed wastewater characterized by ICP-MS show that calcium concentration is about 1.3 g/L, thus the feed wastewater can be categorized into calcium-rich wastewater. The sources of calcium are thought to be associated with textile wastewater processed with lime, detergents, dyes and additives. At given calcium and alkalinity concentrations, temperature, and ionic strength as shown in Table 1, the Langelier Saturation Index was estimated to about 2.2, indicating that the feed water should have high potential of a sparingly soluble salt originated from calcium species.

Microscopic observations of inorganic fouling

At the end of pilot-scale operation of submerged MBR, a coupon of membranes were taken from the hollow-fiber membranes to investigate inorganic fouling by applying microscopic techniques. Scanning Electron Microscope (SEM) was applied to investigate inorganic fouling on the membrane. As shown in Figure 1, the membrane fouling

undoubtedly occurred on the membrane surface and there was considerable evidence of inorganic scaling. The foulnat layer appears to have a stratified crystal structure and forms external fouling on the membrane surface. Using T-EDXA techniques for the identification of each inorganic chemical in the foulant layer, it was observed that the most prevalent inorganic ion in the foulant layer was calcium. Calcium-containing precipitates are very likely because of precipitation of the sparingly soluble salt on the membrane. In the case of the bare membrane, the order prevalence shifts to favour fluoride (F) instead of calcium. The predominance of fluoride can be explained by the component of PVDF membrane tested in this study.

Cross-sectional observations of fouled membrane by SEM (Figure 2) confirmed clearly that the inorganic fouling should contribute to the cake layer significantly on the membrane surface where strong bind and solidification led to external fouling. The T-EDXA results for cross-sectional observation showed that calcium was the main component in the cake layer. The formation of inorganic scaling such as calcium carbonate can be responsible for a reduction in calcium concentration in MF permeate stream, which increases the rejection of calcium (more than 90%). However, the T-EDXA results also show that the presence of calcium within membrane pores is almost negligible, implying that the calcium should be rejected as external fouling on the membrane surface rather than internal fouling within membrane pores. This can be supported further by the T-EDXA taken at position #5 (Figure 2). At this position, most prevalent inorganic ion was observed to be fluoride which is a major component of PVDF membrane materials. In addition, a thick layer of membrane scaling on the membrane surface suggests that the physical scouring generated by the aeration from the bottom of the reactor should not play a significant role on the removal of membrane scaling.

Table 1 | Characteristics of feed wastewater

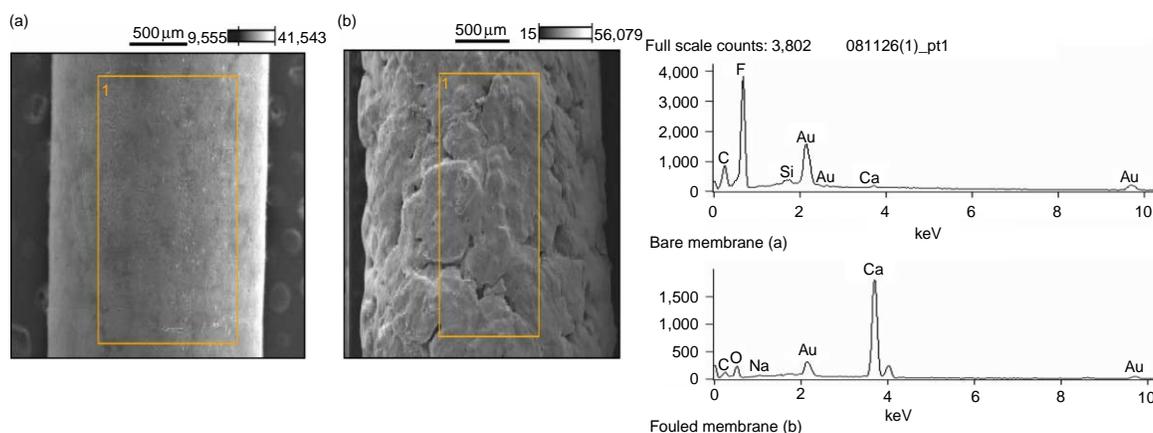|		Component	mg/L	Component	mg/L
pH	7–8	Li	0.04	K	37
Alkalinity (mg/L as $CaCO_3$)	500	Na	161	Mn	0.09
Conductivity (μmhos/cm)	1,000	Mg	3.5	Fe	9.8
Ionic strength (M)	0.016	Ca	1,300	Cu	0.03

Figure 1 │ SEM observations and targeted-energy dispersive analyses of clean (a) and fouled (b) membrane.

FTIR analysis

The FTIR spectra obtained from foulant samples removed from the fouled membrane, chemically- cleaned membrane and bare membrane are shown in Figure 3. Chemical cleaning was conducted sequentially by applying sodium hypochlorite and citric acid solutions (3,000 ppm). As shown in Figure 3, the fact that the FTIR spectra are almost the same for both bare membrane and chemically-cleaned membrane indicates that the basic-acid cleaning should be effective on the removal of membrane scaling. All of the spectra show the same strong adsorption peaks at 1279 and 840 originated from β-form of PVDF membrane and $C-H_2$ rocking for both virgin and chemically- cleaned membrane, respectively (Boccaccio *et al.* 2002). The FTIR peaks at 1396 and 872 are characteristics of the carbonate

due to internal vibration of carbonate ions, supporting that the membrane scale should be calcium carbonate. The FTIR result also shows that the $C-O$ from alcohol in poly-saccharide is observed at $1,010-1,080\,cm^{-1}$. This broad peak increased in the range of wavelength is thought to be polysaccharide or polysaccharide-like substances (Her *et al.* 2000), which will be discussed more below.

Efficiency of chemical cleaning on the removal of membrane scaling

The efficiency of chemical cleaning for the removal of calcium carbonate was evaluated by comparing different sequences of two chemical cleaning solutions (NaOCl and citric acid). It has been generally known that the acid
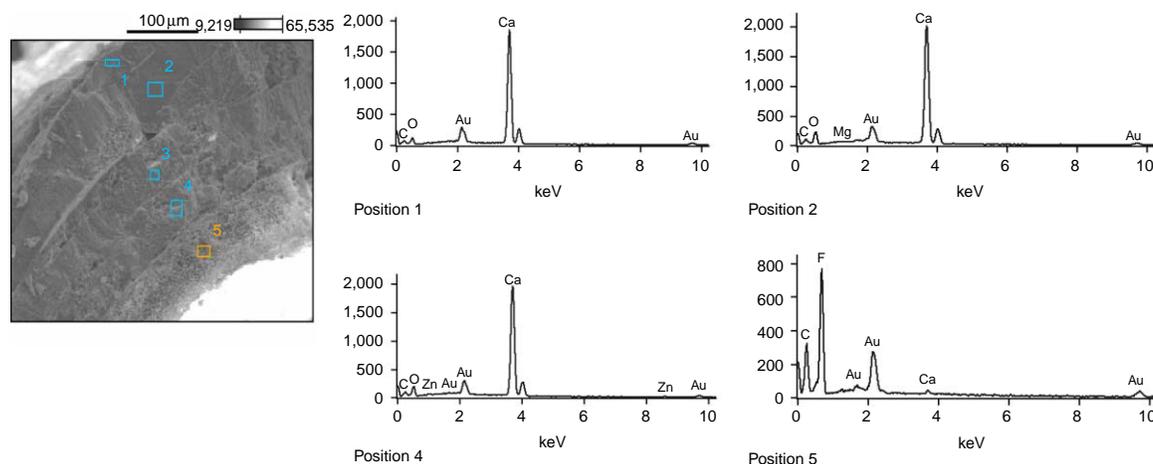

Figure 2 │ SEM observations and TEDA of fouled membrane at different positions in cross-sectional direction.
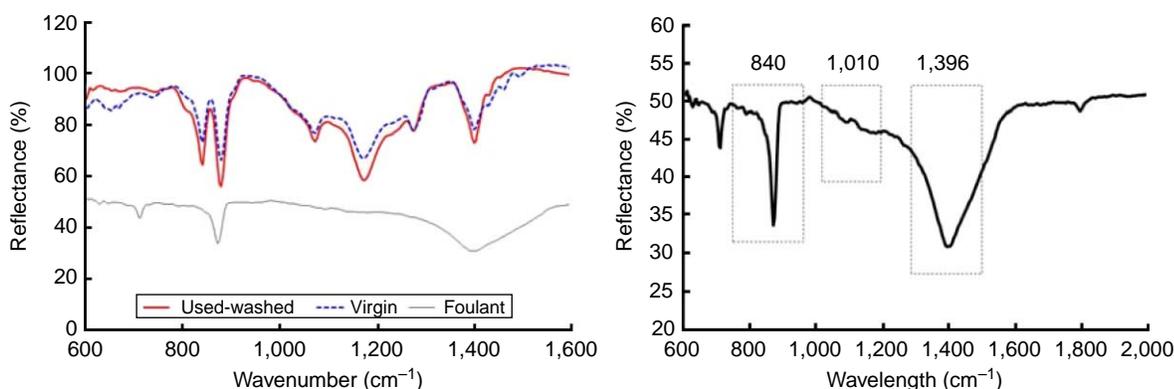
Figure 3 | FTIR spectra for virgin membrane, chemically cleaned membrane and foulant removed from the membrane (left), and enlargement of FTIR peak for the foulant (right).

solution is an effective cleaning agent for the removal of inorganic fouling such as membrane scaling. However, our results show that addition of NaOCl prior to the citric acid could provide better removal of calcium from the membrane (Figure 4). For the calcium-rich wastewater tested in this study, inorganic precipitates such as calcium carbonate have a strong tendency to deposit on the membrane surface as we observed in this study. As shown in Figure 4, the calcium concentration in the eluate obtained when applying sodium hypochlorite prior to the citric acid is much higher (350 mg/L) than one obtained from the opposite sequence (200 mg/L), suggesting that the order of chemical cleaning should be evaluated for optimizing chemical cleaning strategies.

While further works are needed to quantify organic fouling, our explanation is that the foulant on the membrane includes calcium-organic complex, co-precipitation of
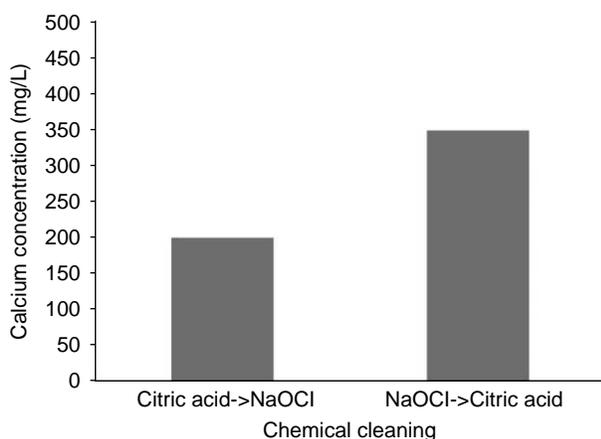
organics with calcite or adsorption of organics onto calcite (Her *et al.* 2000). The oxidative ability of sodium hypochlorite may lead to a loose organic fouling layer because the amount of carbon bonds can be decreased. Strugholtz *et al.* (2005) observed that the best cleaners of organic compounds were NaOCl combined with NaOH followed by HCl in submerged MF water treatment system. The acidic cleaning alone was not suitable for organic removal. They also found that the aromaticity of organics (e.g. humic substances) was decreased by decreasing the amount of double bonds, suggesting that the oxidative reaction due to NaOCl should be indicative. Liu also suggested the oxidative reaction by applying NaOCl should be more efficient at higher pH and the structure of organics becomes linear, which leads to a loose fouling layer (Liu *et al.* 2001). These previous studies can support our results demonstrating that higher calcium concentration in eluate is obtained from applying NaOCl-citric acid than citrtic acid-NaOCl sequence. Applying NaOCl prior to the addition of citric acid allows calcium ions to be released from the calcium-organic complex in the fouling layer more efficiently. As a result, it can be expected that sequence base-acid cleaning enhances the chemical cleaning efficiency because they have the ability to remove organic compounds and inorganic scaling more effectively.

CONCLUSIONS

Membrane autopsy works of MF hollow-fiber membrane in submerged, aerobic MBR treating calcium-rich wastewater provided evidence of significant deposition of calcium

Figure 4 | Calcium concentrations in eluates after chemical cleanings.

carbonate on the membrane surface. The inorganic fouling of calcium carbonate resulted in the cake layer which is strongly attached on the membrane surface. The physical scouring due to aeration generated at the bottom of the reactor did not play an important role in the removal of calcium carbonate. The fact that a large portion of the calcium that could pass through the MF membrane pores was rejected on the membrane surface supported that calcium was rejected as calcium carbonate on the membrane surface. It was also found that the efficiency of chemical cleaning by applying citric acid to remove calcium carbonate could be enhanced significantly by the addition of sodium hypochlorite prior to the addition of the acid cleaning agent. Therefore, chemical cleaning strategies must be evaluated for optimizing the removal of membrane scaling in the aerobic MBR particularly treating wastewater containing high concentrations of calcium.

ACKNOWLEDGEMENTS

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