Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsst20

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H. S. You [a b], C. P. Huang [b], J. R. Pan [b] & S. C. Chang [a]

[a] Industrial Technology Research Institute (ITRI)/Energy and Environment Research Laboratories, Hsinchu, Taiwan

[b] Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan

Published online: 15 Feb 2007.

To cite this article: H. S. You, C. P. Huang, J. R. Pan & S. C. Chang (2006) Behavior of Membrane Scaling During Crossflow Filtration in the Anaerobic MBR System, Separation Science and Technology, 41:7, 1265-1278, DOI: 10.1080/01496390600632487

To link to this article: http://dx.doi.org/10.1080/01496390600632487

Separation Science and Technology, 41: 1265–1278, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600632487

Behavior of Membrane Scaling During Crossflow Filtration in the Anaerobic MBR System

H. S. You
Industrial Technology Research Institute (ITRI)/Energy and Environment Research Laboratories, Hsinchu, Taiwan and Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan

C. P. Huang and J. R. Pan
Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan

S. C. Chang
Industrial Technology Research Institute (ITRI)/Energy and Environment Research Laboratories, Hsinchu, Taiwan

Abstract: Fouling of membrane bioreactor (MBR) has been studied intensively. Because of the high concentration of carbonates, scaling can be a serious problem in anaerobic bioreactor, which attracts little attention. In this study, the wastewater was treated with an anaerobic process followed by either a submerged or a side-stream aerobic membrane reactor. The wastewater was spiked with calcium to investigate the effect of scaling on membrane filtration. Very little scaling was detected in the external membrane system (the side-stream MBR). Results from chemical cleaning of internal membrane system indicated that the flux decline caused by membrane scaling was far more severe than that by membrane fouling. However, the flux decline from membrane scaling can be effectively recovered by the chemical cleaning of EDTA and NaOCl.

Keywords: Membrane bioreactor, scaling, fouling, chemical cleaning

Received 10 January 2006, Accepted 20 March 2006
Address correspondence to C. P. Huang, Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan. Tel: +886-3-5726463; Fax: +886-35-725958; E-mail: cphuang@mail.nctu.edu.tw

INTRODUCTION

Membrane bioreactor (MBR) is a new technology combining a bioreactor and a membrane filtration unit for the separation of biomass, of which the merits have been discussed intensively (1–3). Because nearly all biomass can be retained within the reactor, MBR can maintain a stable and high quality effluent (3). One more advantage of MBR is that it can be operated with long solids retention time (SRT), which is especially beneficial to slow-growing microorganisms (4). As a result, decomposition of refractory organic compounds can be achieved even under short hydraulic retention time (HRT) (5). Although MBR has many advantages, membrane fouling hinders its application tremendously (6). Membrane fouling not only results in reduced flux which demands more frequent membrane cleaning but also shortens the membrane life. Therefore, most research on MBR concentrate on controlling membrane fouling (7, 8).

Most MBRs are operated in aerobic condition. However, anaerobic MBRs have also been studied (9, 10). Unless the permeate is recycled, most anaerobic MBRs must be followed by another aerobic treatment unit to meet the discharge standard. To date, there has been little research studying aerobic MBRs associated with anaerobic units (11, 12).

Besides CO_2 and water, anaerobic biodegradation also produces CH_4. Because the aerobic digester is an open tank, the CO_2 concentration at the top of it is identical to atmospheric CO_2, 0.03%. The anaerobic tank, on the other hand, is enclosed and is operated at 30 to 50 cm hydraulic head. Therefore, the gaseous space of the anaerobic tank contains 20 to 40% CO_2 and 60 to 80% CH_4. As a result of the increased CO_2 partial pressure, the solubility of CO_2 is much higher than usual. Thus, in order to maintain a neutral pH environment for microorganisms, alkalinity in the anaerobic tanks must be supplemented, increasing the concentration of carbonate ions. When the effluent of the anaerobic reactor flows into the aerobic reactor, the supersaturated CO_2 is released and the pH of the liquid phase rises substantially. In addition, the carbonates of metals such as Ca, Mg, and Fe crystallize, increasing the potential of membrane scaling (12).

The resistance-in-series model has been widely used to describe the filtration behavior of membranes (13):

$$J = \frac{\Delta P_T}{(\eta \cdot R_t)} \tag{1}$$

$$R_t = R_m + R_c + R_f \tag{2}$$

where J is the permeation flux, ΔP_{T} is the transmembrane pressure (TMP), η is the viscosity of the permeate; R_{t} is the total resistance; R_{m} is the intrinsic membrane resistance; R_{c} is the cake resistance formed by the cake layer resistance; and R_{f} is the resistance caused by solute adsorption into the

membrane pores and walls. For a MBR susceptible to scaling, the R_f and R_t must be adjusted:

$$R_f = R_{org-f} + R_{inorg-s} \quad (3)$$

$$R_t = R_m + R_c + R_{org-f} + R_{inorg-s} \quad (4)$$

where R_{org-f} is the resistance caused by organic adsorption into the membrane pores and walls; $R_{inorg-s}$ is the resistance caused by inorganic scaling in membrane pores and on walls.

Membrane fouling is a result of the reaction between the membrane and particles in the suspension. The floc-structure of the activated sludge, particle size distribution, and extracellular polymeric substances (EPS) content of the activated sludge are all related to membrane fouling (7). EPS is either produced by the microorganisms or the decomposition products of the dead cells. It bears a negative charge at neutral pH due to the functional groups of carboxyl, amino, and phosphate (4).

Carbonate compounds, on the other hand, bear a slight positive charge. The bioflocs will adsorb the carbonate crystals through charge neutralization, and the potential to foul or scale on the membrane is greatly reduced through a mechanism called bio-flocculation (14). The aim of this research is to investigate the effect of fouling and scaling on membrane filtration during MBR operation and the efficiency of chemical cleaning in the recovery of membrane flux. This MBR follows the anaerobic reactor that the carbonate crystals have the higher potential to form than normal aerobic MBR.

EXPERIMENTAL

Design of the MBR Process

The schematic of the MBR process is shown in Fig. 1, which follows an Upflow Anaerobic Sludge Bed (UASB). The influent substrates of UASB were composed of glucose and acetic acid. The influent COD of UASB ranged from 12,000 to 16,000 mg/L. The effluent of UASB, with 1500 to 2500 mg/L COD, pH of 6.8 to 7.2, and alkalinity between 1500 and 2000 mg/L as $CaCO_3$, overflowed into a mixing tank in which the desired amount of $CaCl_2$ was added. Two types of MBRs were designed to test the effect of the relative location of the membrane module to the bioreactor on scaling. One was the internal submerged MBR (internal membrane system), of which the membrane module was placed inside the bioreactor. The other one is the external submerged MBR (external membrane system), of which the membrane module was separated from the biological reactor. The volume of the biological reactor of the external membrane system was 20 L, and the membrane tank was 8 L.

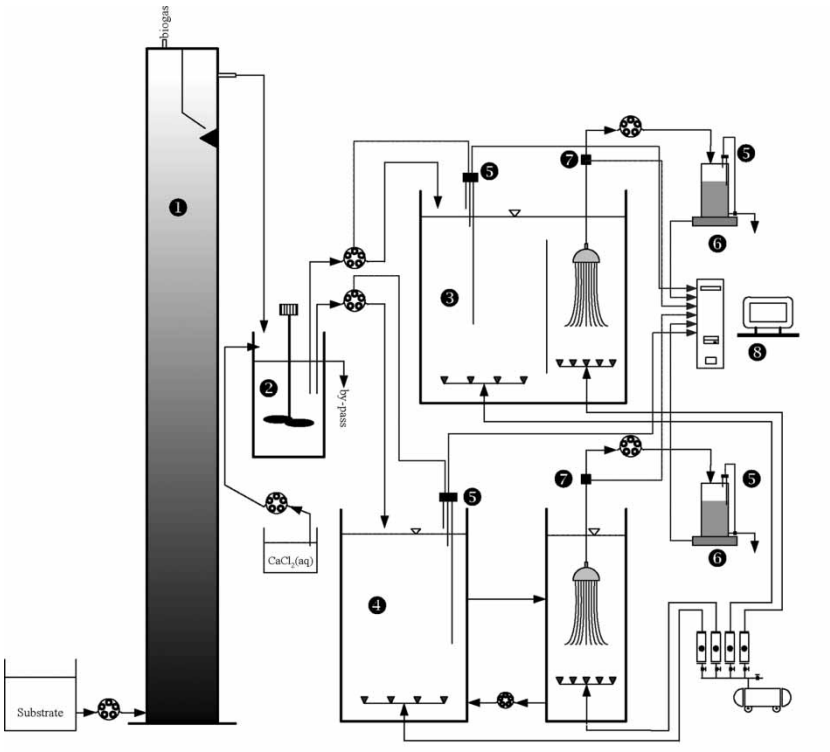

Figure 1. Schematic diagram of the experimental setup.

The total volume of the internal membrane system was 28 L. The reactor was partitioned into two cells: the reactor area (20 L) and the membrane area (8 L). The flow rate of the sparging gas was 1 m/sec (15). No back-feeding flushing was performed during the entire period of membrane operation. The aeration rate was controlled to satisfy the biochemical reaction of the bioreactor.

The feeding during membrane operation was controlled by the liquid level controller. The permeate was accumulated in a buffer tank with balance, liquid level controller and magnetic valve to calculate the flux. The amount of the permeate and the TMP were monitored automatically by a computer with the SCADA (Supervisory Control And Data Acquisition) and data analysis. In the external membrane system the recycled flow from the membrane tank to the bioreactor was three times that of the feed into to the bioreactor. The MLSS of both systems were maintained at 8000 ± 500 mg/L. The $CaCl_2$, 50–350 mg/L as Ca, was added after 70 hours of operation. The feed to the

MBR varied with the flux. Therefore, the HRT of the MBR was lengthened with the decline in flux.

Membranes and Module Configuration

The membrane was obtained from Zenon Environmental Inc., and was an immersed ultrafiltration (UF) type of pore size 0.036 μm. The hollow fiber has an inner dia. of 0.9 mm and outer dia. of 1.9 mm. The membrane is resistant to strong acids and bases (operational pH of 3–12) and corrosion by chemicals like OCl^-. To prevent accumulation of microorganisms between fibers, the module was modified from the ZW-1, as shown in Fig. 2. The TMP of the intrinsic membrane was 4 kPa and the membrane surface area was 0.046 m^2. The initial flux was set at 14 L/m^2-hr.

PHYSICAL AND CHEMICAL CLEANING

Cleaning by back-feeding was not adopted during the entire period of membrane operation. When the flux declined to 30% of the original flux, the operation was terminated and the membrane was removed from the

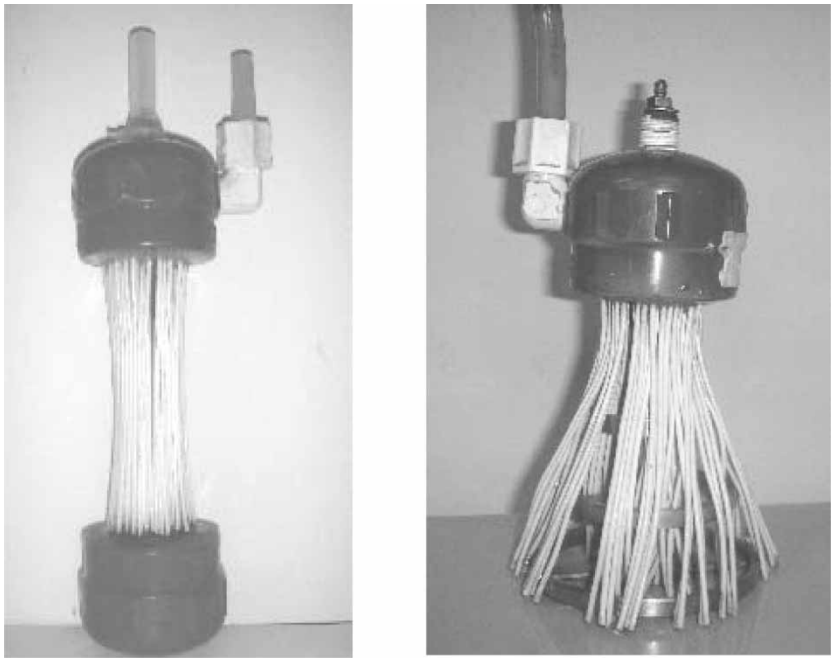

Figure 2. Membrane modules (Left: ZW-1 module; Right: modified module).

bioreactor and placed in the cleaning tank for cleaning, as shown in Fig. 3. During soaking cleaning, in addition to air flushing, the pump was started to remove the permeate. The TMP and the flux were monitored. When the volume of the accumulated permeate reached a predetermined value, the electric valve would open to allow the permeate to flow into the cleaning tank. The cleaning is finished when the TMP and the flux would no longer change with the cleaning time.

Membrane fouling can be attributed to three mechanisms: cake formation, inorganic scaling and organic fouling. In this study, the fouled membrane was cleaned with physical and chemical cleaning process to differentiate the contribution of each mechanism to membrane fouling. First, the membrane was clean with DI water and air flushing. The air rate was 2 m/sec, twice the flow rate of the sparging gas. The reduction in TMP after the physical cleaning was attributed to the cake formation. The cleaning was followed by the chemical cleaning of EDTA solution and air flushing. The flow rate of the air was 2 m/sec, and 2000 mg/L EDTA was added. The reduction in TMP after this step was attributed to inorganic scaling. The last step was the chemical cleaning by NaOCl solution and air flushing. The flow rate of the air was 2 m/sec, and 2000 mg/l NaOCl as OCl^- was added to dissolve the organic fouling. The reduction in TMP after the chemical cleaning by NaOCl was attributed to organic fouling.

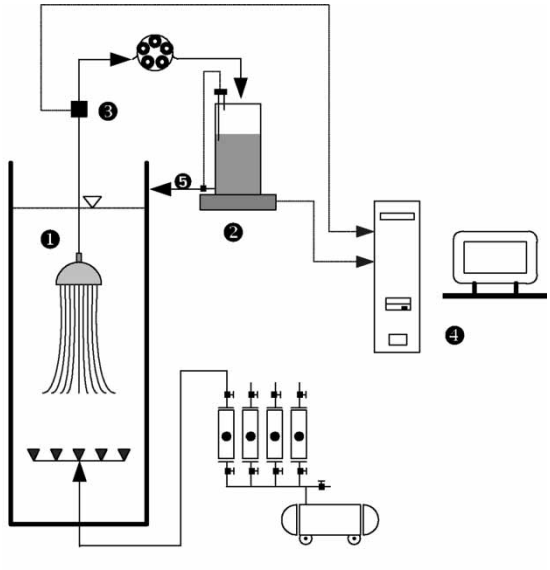

Figure 3. Physical and chemical cleaning equipment.

Assessment of Membrane Performance

During MBR operation, the calcium ion concentration in the influent and the permeate were analyzed with an atomic absorbance spectrophotometer (Varian Spectra AA-30). After the operation, the membrane was removed from the membrane module and the chemical composition of the scaling was analyzed by a scanning electron micrograph—energy dispersive spectrometry (SEM–EDS, Oxfoxd, ISIS 300); the inorganic scaling was analyzed with X-ray Diffraction (Bruker AXS D8 ADVANCE).

RESULTS AND DISCUSSION

Scaling of the Two MBR Systems

The scaling of the two MBR systems was magnified by the seeding of Ca. The influent of MBR which is generated from the UASB contained 1500 to 2500 mg/L COD, and the COD of the permeate remained between 50 to 100 mg/L during the entire course of operation. The pH of the influent was approximately 6.8–7.2 which increased slightly to approximately 8.2–8.5 in the bioreactor due to the stripping of CO_2. The initial flux of both MBRs was set at 14 L/m^2-hr. At the beginning of the operation, no Ca was added. After 70 hours of operation, various amounts of $CaCl_2$, namely, 50 and 350 mg/L as Ca, were added. The variation of Ca concentration in the permeate is shown in Fig. 4. Although the Ca concentration of the permeate increased with the increasing Ca concentration of the influent, the correlation between the two systems were similar and the permeate Ca concentration was between 20 and 80 mg/L as Ca.

The variations of flux and TMP during MBR operations are shown in Fig. 5. Both Figs. 5(a) and (b) show that the flux and the TMP stayed fairly constant in both systems before the addition of Ca. Dramatic discrepancy was observed between the two systems after the addition of calcium. In the internal membrane system, as shown in Fig. 5(a), two phases of change were observed. In the first phase, the TMP increased gradually from 7 to 20 kPa, while the flux decreased from 14 to 11 L/m^2-hr. In the second phase, the TMP increased abruptly to 50 kPa with a sudden flux decline to 4 L/m^2-h, which led to chemical cleaning because of the reduction of over 70%. On the other hand, the effect of $CaCl_2$ addition on the flux and TMP of the external membrane system was minor, as shown in Fig. 5(b). It implies that the external membrane system is probably a better choice when scaling-causing metal ions are present.

Scaling was a complicated process, including crystallization and hydrodynamic transport (16). Two mechanisms involved in crystallization are bulk (homogeneous) and surface (heterogeneous) crystallizations (16, 17). In bulk crystallization, supersaturated brine gives rise to the agglomeration

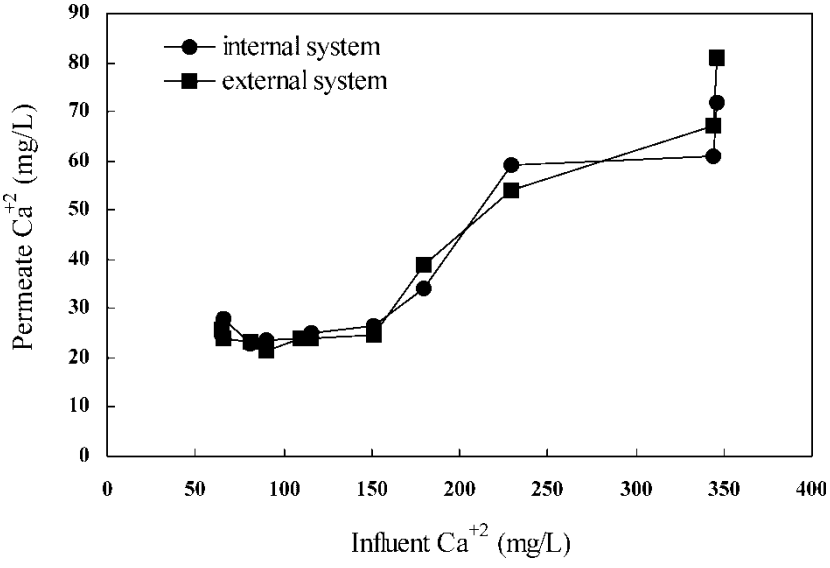

Figure 4. Ca^{2+} concentration of permeate as a function of different influent Ca^{2+} concentration.

of scale-forming ions due to random collisions of the ions in motion. The cluster of ions coalesces to form a crystal inducing precipitation upon reaching a critical size. On the other hand, surface crystallization may be caused by foreign bodies such as the membrane surface itself. As a result, membrane fouling occurs by the deposition of a crystal particle formed in a bulk phase and/or the lateral growth of crystals on a membrane surface. To prevent membrane scaling, both clusters of ions or free ions and the crystals must be free from contact with the membrane.

In the membrane system, aeration in the bioreactor stripped CO_2 from the liquid phase resulting in an increase in pH and the formation of Ca crystals bearing a slight positive charge. The bioflocs in the bioreactor are negatively charged due to functional groups such as $-COOH$, $-NH_2$ and $-PO_4$. Through charge neutralization, Ca crystals as well as free calcium were caught by the flocs and removed from the liquid phase. In the external membrane system, the direct contact of crystals and free cations with the membrane is avoided which prevents future membrane scaling. The bioflocculation between bioflocs and crystals has also been clarified in our previous paper (12, 14).

Furthermore, because of the difference in the aeration rate and sparging rate of the internal membrane system, internal circulation occurs inside the bioreactor. The circulation of the metal clusters or metal ions in the system continuously moves toward the surface of the membrane before they have a chance to react with the bioflocs. The scaling of the small crystals gradually blocked the membrane pore which caused declined flux. When large areas

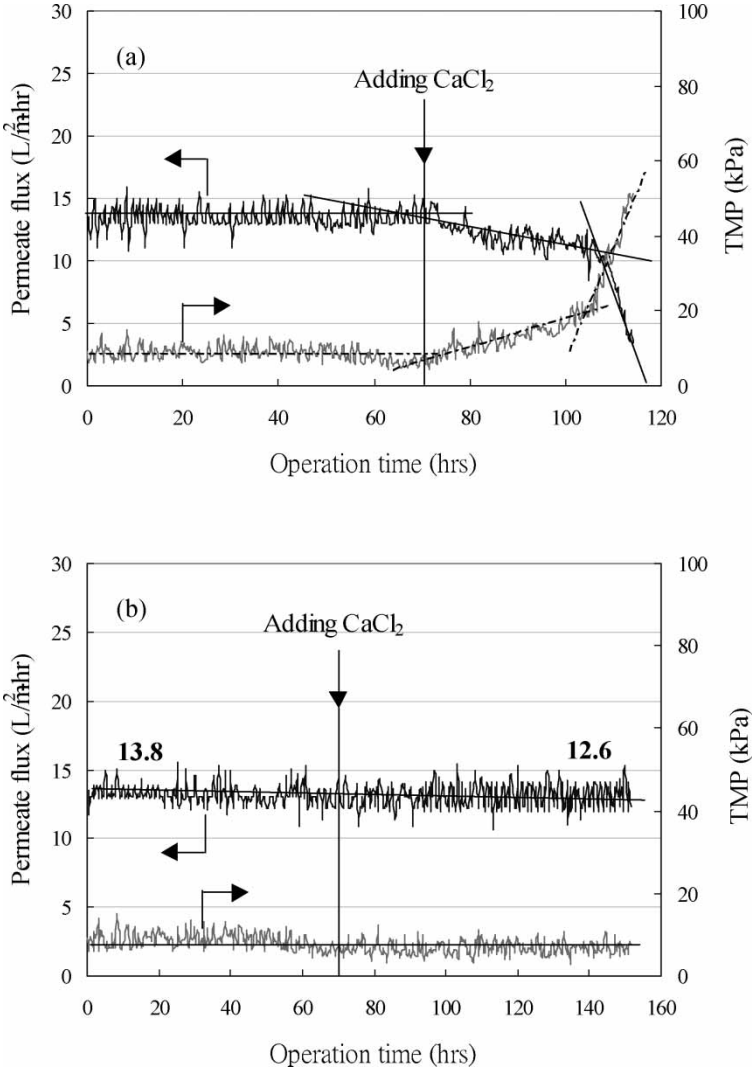

Figure 5. Effect of $CaCl_2$ addition on permeate flux and TMP profiles under different MBR systems. (a) internal membrane system, (b) external membrane system.

of the membrane were blocked, membrane fouling occurred, as seen in the sudden increase in the TMP in Fig. 5(a).

Analysis of the Membrane Surface

After each cycle of operation, the hollow fibers were removed from the membrane module of both MBRs for photographs and mineral identification.

The results are shown in Fig. 6. The surface of the membrane from external membrane system is smooth and free of deposit. The photographs and results of the analysis demonstrate that the membrane from the internal membrane system was covered with crystals. The peak, as seen in Fig. 6(b-2), in the SEM–EDS diagram indicates the scale is a calcium crystal. X-ray diffraction further confirms that the scale on the membrane surface of internal membrane system consists of calcium carbonate (Figure 7).

Physical and Chemical Cleaning

Many researchers have studied the behavior of membrane filtration using the resistance-in–series model, in which potential fouling matter is separated into suspended solids, colloids, and solutes. The cake resistance and fouling resistance of each component are calculated separately (18–20). The disadvantage of this method is that it neglects the interactions between components. In this study, the contributions of inorganic scaling and organic fouling on flux decline were studied by examining the outcome of physical and chemical cleaning.

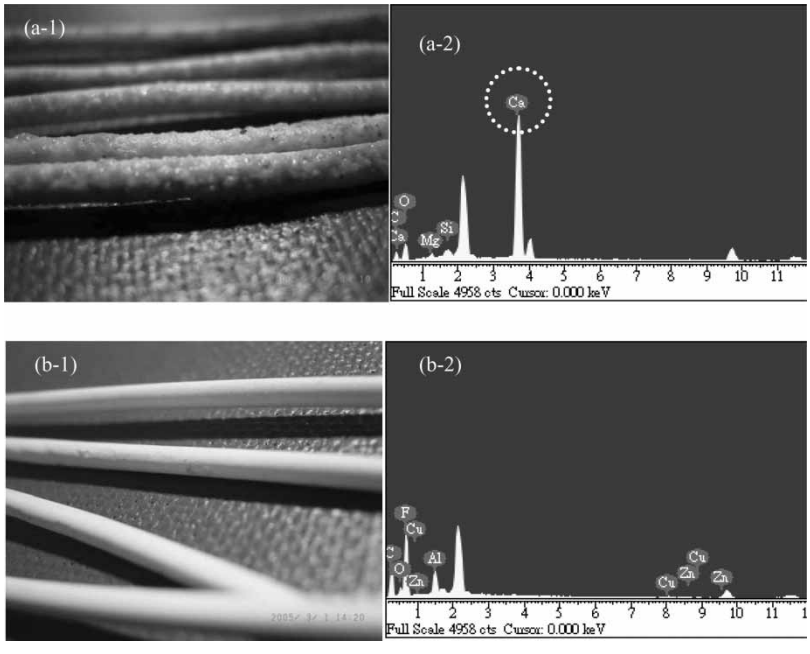

Figure 6. Element analysis of membrane surfaces under different MBRs operations. (a) internal membrane system: (a-1) SEM-EDS analysis and (a-2) membrane photo; (b) external membrane system: (b-1) SEM-EDS analysis and (b-2) membrane photo.

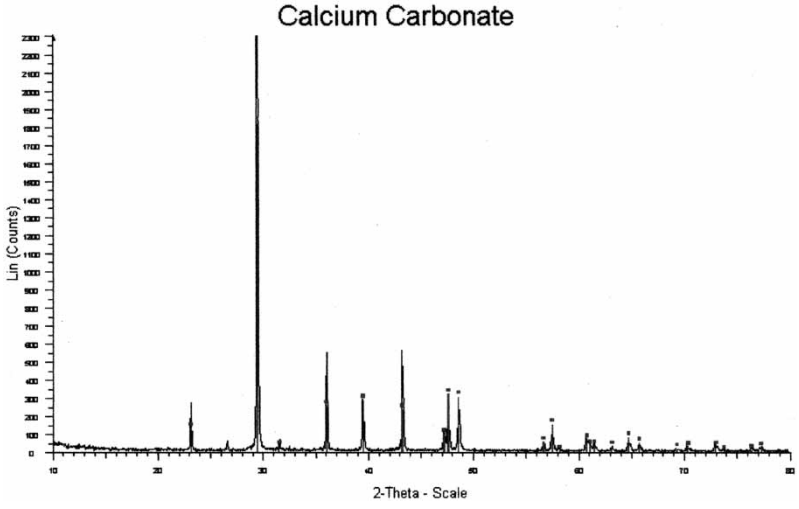

Figure 7. X-ray diffraction spectrum of membrane surface in the internal membrane system. (2θ: 10–80°, step scan: 0.06°/step, step time: 2 second, 40 kV, 40 mA).

Figure 8 shows the variation of TMP and Flux of internal membrane system during physical and chemical cleaning. No change in TMP and Flux was observed during the first six hours of air flushing, indicating no cake formation on the surface of the membrane. The TMP dropped sharply and the flux increased

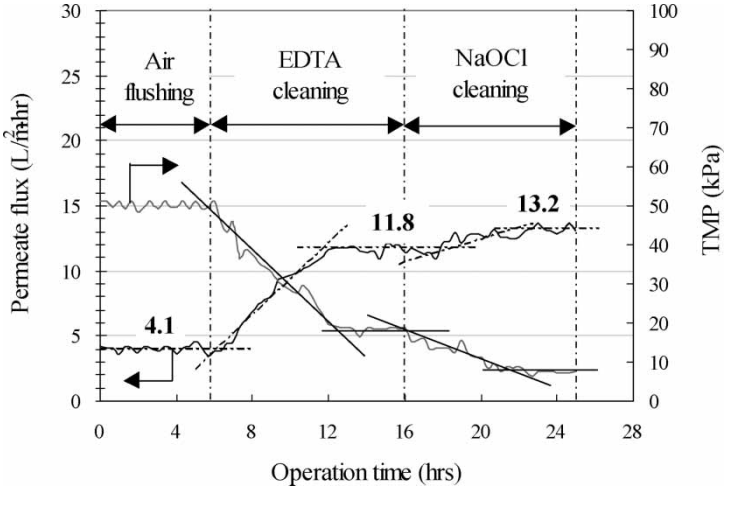

Figure 8. Patterns of permeate flux and TMP during physical and chemical cleaning on internal membrane system. (air flushing: 2 m/sec, EDTA concentration: 2000 mg/L, NaOCl concentration: 2000 mg/L as OCl^-).

Table 1. Flux declines of MBRs with internal and external membrane system

(%)	Total	Cake deposited	Organic fouling	Inorganic scaling
Internal membrane system	100 (14 to 4.1)	Neglect	14.1 (13.2–11.8)	77.8 (11.8–4.1)
External membrane system	100 (13.8 to 12.6)	Neglect	100 (13.8–12.6)	Neglect

[a]8% irreversible fouling.

immediately after the administration of EDTA. No further change was observed four hours after EDTA cleaning. After 16 hours of EDTA administration, cleaning by NaOCl was conducted using 2000 mg/L as OCl^-. In the first six hours of NaOCl cleaning, the TMP reduced gradually accompanied by a slow increase in flux. The final flux was 13.2 L/m^2-hr, or a 94% recovery, indicating that chemical cleaning using a combination of EDTA and NaOCl can efficiently remove inorganic and organic fouling on the membrane surface.

The flux decline contributed by inorganic scaling and organic fouling can be calculated accordingly. Calculation results are summarized in Table 1. In the internal membrane system, 77.8% of flux decline was due to inorganic scaling and 14.1% was due to organic fouling. Out of the total flux decline, 8.1% was irreversible fouling which could not be recovered even by chemical cleaning. In the external membrane system, no chemical cleaning was performed because the flux decline was less than 70%. As shown in Fig. 6, no scaling was formed in the external membrane system. Therefore, all the flux decline was due to organic fouling. Figure 5(b) shows that after 150 hours of MBR operation the flux dropped only slightly from 13.8 to 12.6 L/m^2-hr, the equivalent of a 8.7% decline.

CONCLUSIONS

1. Scaling of membrane can be effectively controlled by MBR with an external membrane system. The MBR with internal membrane system has serious scaling problem.
2. The inorganic scaling and organic fouling can be efficiently removed by chemical cleaning with EDTA and NaOCl.

ACKNOWLEDGEMENT

The authors would like to thank Dr. S.S. Chou and Dr. K.F. Chang of ITRI, and Prof. S.S. Cheng of National Cheng Kung University for their helpful discussions, as well as Miss S. H. Perng for her technical assistance with

chemical analysis. This study was partially supported by the project of Aim to the Top University, MOE.

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