

Characteristics of Soluble Foulants in the Membrane Bioreactor (MBR)

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ABSTRACT

The pilot submerged MBR (PSMBR) was operated with sewage to investigate the characteristics of soluble membrane foulants. Molecular weight distributions of soluble materials were analyzed and molecular weight fractionations were conducted as protein and carbohydrate compositions. Soluble materials of MW above 40 kDa were rejected by membrane, even if 0.4 μm pore size of microfiltration was used. Fourier transform infrared (FTIR) spectra and scanning electron microscope (SEM) were applied to monitor fouled membrane surface. FTIR analysis showed that protein and carbohydrate were dominant on the membrane surface. The cleaning efficiency tests showed that the combination of chemical and physical cleaning strategy was the most efficiency methods in this study.

KEYWORDS: MBR, Molecular weight, Bio-fouling, FTIR, Protein, Carbohydrate

INTRODUCTION

Among the various wastewater treatment technologies, membrane bioreactors (MBR), are considered as one of the most promising processes for wastewater treatment, water reuse and reclamation due to their potential advantages, such as complete removal of solids from an effluent, superior nutrient and organic removals, high loading rate capabilities, low/zero sludge production and small foot print. However, the main problem of the application of MBR is the membrane fouling (Jang *et al.*, 2004).

In MBR process, extracellular polymeric substances (EPS) and soluble microbial products (SMP) are known as major foulants. EPS are of biological origin, participate in the formation of microbial aggregates and consist of insoluble materials (sheaths, capsular polymers, condensed gel, loosely bound polymers, and attached organic material). SMP are soluble cellular components or soluble EPS (soluble macro-molecules, colloids, and slimes) (Lapidou and Rittmann, 2002). EPS and SMP are closely related with cake layer resistance (caused by suspended solids) and pore blocking resistance (caused by soluble materials), respectively, and those are usually caused by suspended solids and soluble materials, respectively (Jang, 2006).

It is reported that membrane fouling caused by suspended solids is only partially responsible, and that soluble materials may be the main contributor, especially, aeration intensity is enough to prevent cake formation on the membrane surface (Jang, 2006). Bouhabila *et al.* (2001) and Wisniewski and Grasmick

(1996) reported fractions of membrane fouling due to suspended solids in the MBR of 23 and 24%, respectively.

Of the various characteristics of soluble materials, molecular weight distribution is critical factor for the rejection of soluble materials by membrane that directly linked with membrane fouling. Also, it is known that main compositions of EPS and SMP are protein and carbohydrate (Frølund *et al.*, 1996; Liu and Fang, 2003).

In this study, a pilot scale MBR was operated with sewage to characterize soluble membrane foulants in the MBR operation. Molecular weight distributions of soluble materials were analyzed and molecular weight fractionations were conducted as protein and carbohydrate compositions. Fourier transform infrared (FTIR) spectra and scanning electron microscope (SEM) were applied to monitor fouled membrane surface.

MATERIALS AND METHODS

Pilot MBR operation

The pilot submerged MBR (PSMBR) was operated with sewage from a dormitory of GIST. The effective volume of the aeration reactor was 2.44 m³, with a submerged microfiltration membrane module (plate and frame type, PVDF, 0.4 μm pore size, Pure-Envitech, South Korea). Permeate was produced at a rate of 10.5 L/m²·hr, in the constant flux mode. Intermittent suction was applied; 7 minutes suction, 3 minutes release. The chemical cleaning was conducted when the trans-membrane pressure reached 200 mmHg, which was achieved using NaOCl. The pH was controlled within the range of 6.8-7.5 with the use of NaHCO₃. The configuration of denitrification was adapted circulating type (circulation from nitrification reactor → denitrification reactor → nitrification reactor) without input and output in the denitrification reactor. The effective volume of the denitrification reactor was 0.87 m³. The circulation flow from the aeration reactor to denitrification reactor was equivalent to the influent flow (Q), with the same flow returning to the aerobic reactor. Methanol was added as external carbon source (COD/N = 5) to the denitrification reactor, and the circulation flow was fixed as 2Q.

Table 1. Operating conditions of the pilot MBR.

Item	Unit	Average value
Volumetric loading rate	g COD/l·d	0.64
Hydraulic retention time	hour	10.6
Solid retention time	day	20
Biomass concentration	g VSS/l	3.7
F/M ratio	g COD/g VSS·d	0.13
Total nitrogen removal rate	%	77
COD removal rate	%	96

Molecular weight analysis

The molecular weight distributions of the soluble materials was measured by high performance size exclusion chromatography (HP-SEC) using UV (SPD-10A vp, UV-vis detector, Shimadzu, Japan), fluorescence (RF-10A x1, Shimadzu, Japan), and DOC (Sievers 820, Boulder, CO, US) detectors. Both the fluorescence and DOC detectors were used to measure the molecular weight distributions.

Centrifugal membrane devices, with 1 k and 10 kDa cutoff values, (Microsep, PALL Corporation, USA) were used for the molecular weight fractionations of soluble materials. The filtration device was centrifuged for 99 minutes at 7,000 g (VS-21SMT, Vision Scientific, Korea).

Membrane surface analysis

Fourier transform infrared (FTIR) spectra were measured using a JASCO spectrometer (FTIR-460 plus, JASCO Inc., Japan). The IR Mentor Pro™ software, 6.5 version (Bio-Rad Laboratories, USA), was used to find the FTIR peaks that related to specific chemical bonds. A picture of the membrane surface was taken using a scanning electron microscope (SEM, S-4700, Hitachi, Japan).

Analysis

The carbohydrate and protein concentrations of the supernatant were measured using the methods of Dubois *et al.* (1956) and advanced protein assay reagent (Cytoskeleton, USA), respectively. Bovine serum albumin (BSA), and dextrose were used as the protein and carbohydrate standards, respectively. The MLSS and MLVSS (Mixed Liquor Volatile Suspended Solids) concentrations were measured following the Standard Methods (APHA, 1998). The particle size distribution was measured with a laser particle size analyzer (LS-230, Beckman Coulter, USA). The COD (Chemical Oxygen Demand) and total nitrogen (T-N) were analyzed using a Humas kit (KIT, Humas, Korea).

RESULTS AND DISCUSSION

Molecular weight distributions of soluble materials

Figure 1 shows the molecular weight (MW) distributions of soluble materials in the influent, bioreactor and permeate at steady state of the PSMBR. The permeate result indicated that soluble materials of MW above 40 kDa were adsorbed on the membrane pore or rejected by membrane, even if 0.4 μm pore size of microfiltration was used in this study. It was assumed that the gel layer formed by concentrated soluble materials or bio-cake layer formed by suspended solids on the membrane surface played a role of secondary membrane.

Molecular weight fractionations as protein and carbohydrate

Figure 2 shows the characteristics of the soluble protein as MW fractionations in the influent, nitrification

reactor [bioreactor (N)], denitrification reactor [bioreactor (D)] and permeate at a steady state. The error bars show the standard deviation. About 93% of the soluble protein contained in the influent existed above a MW of 10 kDa. The result in permeate showed that the portion above a MW 10 kDa of protein slightly decreased after membrane rejection.

Figure 3 shows the characteristics of the soluble carbohydrate as MW fractionations at a steady state. The soluble carbohydrate showed higher concentrations than the protein SMP. About 88% of soluble carbohydrate contained in the influent existed above a MW of 10 kDa. The result in the bioreactor (N) indicated that the carbohydrate below a MW of 1 kDa was produced via aerobic biological reactions. Also, the result in permeate showed that the concentration and portion above a MW 10 kDa of carbohydrate slightly decreased after membrane rejection.

The soluble protein concentration in the denitrification reactor was higher than that in the nitrification reactor (Figure 2). The fraction of high MW of soluble carbohydrate in the denitrification reactor was higher than that in the nitrification reactor (Figure 3). It was assumed that the floc deterioration caused EPS release to the SMP as described previous works (Jang *et al.*, 2005).

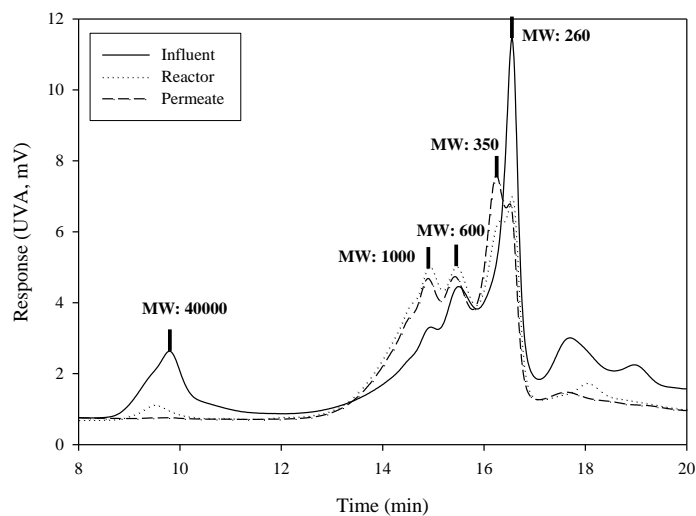


Figure 1. Molecular weight distributions of soluble materials in the pilot MBR.

Membrane surface analysis

FTIR (Fourier transform infrared) spectra analysis was conducted to characterize soluble foulants on the surface of the membrane. The membrane surface was washed by deionized water to detach the bio-cake on the membrane surface before the analysis. Figure 4 shows the FTIR results of pure and fouled membrane. It is known that peaks near 1050 cm^{-1} (C-O), and near 1540 cm^{-1} (C-N-H) and 1660 cm^{-1} (H-N-H), are indicative of carbohydrate character and of protein, respectively (Kimura *et al.*, 2004). FTIR analysis indicated that protein and carbohydrate were dominant on the fouled membrane surface.

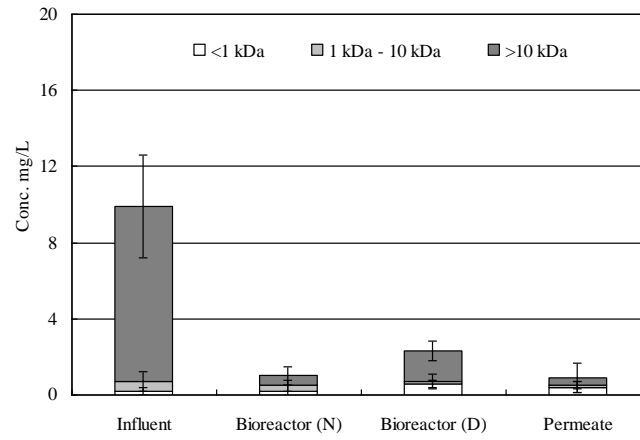


Figure 2. The molecular weight fractionations of the soluble protein.

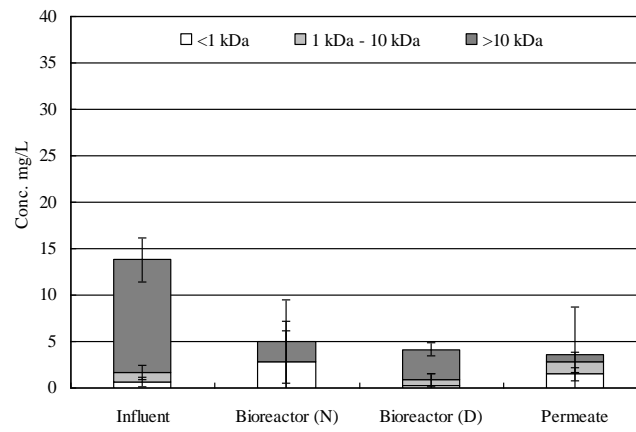


Figure 3. The molecular weight fractionations of the soluble carbohydrate.

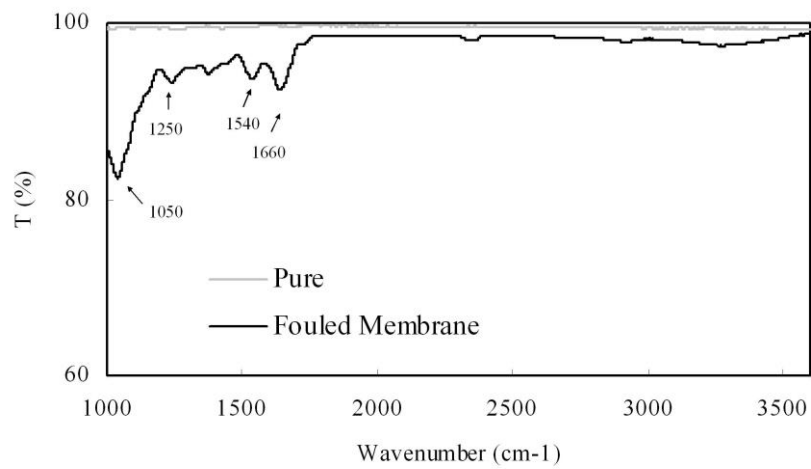


Figure 4. FTIR results of pure and fouled membrane.

Figure 5 shows the SEM images of the same sample of membrane surface that was used for FTIR analysis. Circular pores were observed in the pure membrane (Figure 5 a and b), while the pores were completely covered by foulants before chemical cleaning (Figure 5c). The membrane surface after chemical cleaning (simple dipping to the 1,000 ppm NaOCl solution during 2 hours) showed some recoveries of the pores (Figure 5d). However, the simple chemical reaction was assumed to be not satisfied for the flux recovery.

The cleaning efficiency test was conducted for the cleaning strategy in the PSMBR. The membrane samples were cut as the size of 1 cm x 5 cm. Four batch assays (Pure water dipping, 200 rpm mixing, 5,000 ppm NaOCl dipping and NaOCl with mixing) were prepared and tests were conducted room temperature (20°C). The FTIR residual peaks (residual / initial peaks) were compared after the 12 hours of batch tests.

Figure 6 shows the results of cleaning efficiency test. The results showed that the combination of chemical and physical cleaning strategy was the most efficiency methods in this study. Without chemical or physical cleaning method, pure water dipping assay showed 25-40 % reduction of carbohydrate and protein peaks. Residual peaks of mixing assay were lower than those of NaOCl dipping assays except protein peak of 1540 cm^{-1} (C-N-H). The carbohydrate peak of 1050 cm^{-1} (C-O) was the hardest peak to remove in the cleaning efficiency test. In this study, the membrane was brushed with sponge media that was dipped to the NaOCl solution (physical + chemical strategy) for the membrane chemical cleaning.

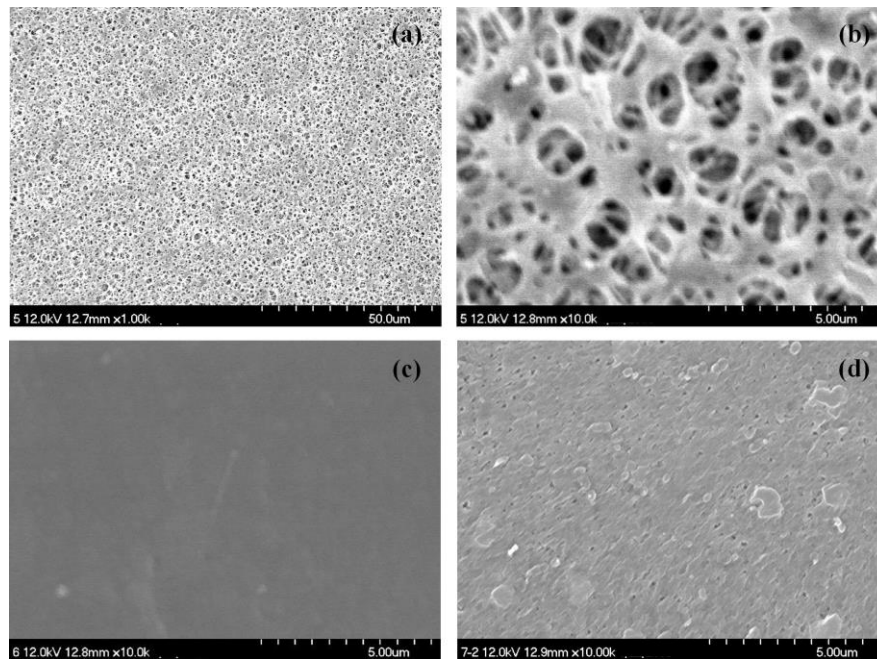


Figure 5. SEM images of the plate and frame membrane surface in the PSMBR.

[a: pure membrane (x1,000), b: pure (x10,000), c: fouled (x10,000), d: cleaned (x10,000)]

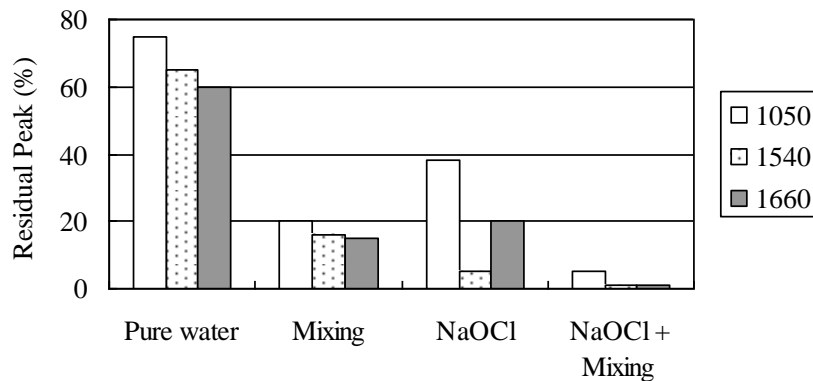


Figure 6. FTIR residual peaks in the cleaning efficiency test.

CONCLUSIONS

In this study, the pilot submerged MBR (PSMBR) was operated to investigate the characteristics of soluble membrane foulants. The following conclusions were drawn.

1. Molecular weight distributions of soluble materials showed that soluble materials of MW above 40 kDa were adsorbed on the membrane pore or rejected by membrane, even if 0.4 μm pore size of microfiltration was used in the PSMBR.
2. The permeate result of MW fractionation showed that the portion above a MW 10 kDa of protein and carbohydrate slightly decreased after membrane rejection. The result in the bioreactor indicated that the carbohydrate below a MW of 1 kDa was produced via aerobic biological reactions.
3. FTIR analysis showed that protein and carbohydrate were dominant on the membrane surface.
4. The cleaning efficiency tests showed that the combination of chemical and physical cleaning strategy was the most efficiency methods in this study.

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