Journal of Environmental Biotechnology
Vol. 16, No. 1, 65–68, 2016

Technical Paper

A Preliminary Diagnostic Method for Membrane Fouling Using Extracellular Proteins Secreted in Pilot-Scale Membrane Bioreactors

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(Received: 30 May, 2016/Accepted: 8 July, 2016)

Key words: membrane bioreactor, membrane fouling, extracellular protein, wastewater treatment, activated sludge

1. Introduction

Membrane bioreactors (MBRs) are advanced tools for biological wastewater treatment to obtain high-quality treated water using ultrafiltration or microfiltration membranes for solid–liquid separation[2]. Despite their advantages over the conventional activated sludge method, a major challenge associated with the use of MBRs is membrane fouling, which involves the clogging of membrane pores due to the attachment and accumulation of microorganisms, microbial products (e.g., extracellular proteins, polysaccharides, and lipids), and other organic/inorganic components on membrane surfaces. Membrane fouling results in an increase in transmembrane pressure (TMP), a severe decline in flux, and a reduction in treatment performance, causing high energy consumption. Although a number of studies have focused on controlling membrane fouling, some of which achieved progress in this regard, the complete prevention of fouling has not been possible. Therefore, membrane cleaning by physical and chemical treatment at periodic intervals is essential for the stable operation of MBRs[4].

Membrane fouling can be divided into different types based on the strength of attachment of the fouling materials or foulants to the membranes[12]. Reversible membrane fouling likely stemming from the loose attachment of foulants is resolved by physical cleaning methods, but it can transform into irreversible fouling by the formation of layered strong fouling matrices during continuous long-term filtration. Removal of these recalcitrant foulants cannot be achieved by physical cleaning, but can be done by chemical cleaning. In chemical treatment, a variety of washing agents, such as acids, bases, chelating agents, polymeric coagulants, surfactants, and oxidants, including sodium hypochlorite, have been employed[3,8]. However, over time, conventional chemical cleaning becomes only partially effective against irreversible fouling and the completely fouled membrane has to be replaced; this is frequently required[12].

Despite intensive efforts, the fundamental mechanism underlying membrane fouling remains to be clarified[1]. Membrane fouling of MBRs is usually detected by an increase in the TMP; however, the sensitivity of detection of increased TMP is insufficient to evaluate and prevent its occurrence. In practice, early prediction of the precise timing of membrane fouling and when chemical cleaning of a fouled membrane should be performed are important. Thus, alternative methods for effectively predicting membrane fouling prior to the increase of TMP need to be developed.

In addition to microbiologically produced polysaccharides, proteins have been identified as one of the major foulants of MBRs[5,6], and some proteins that cause membrane fouling were identified in pilot-scale MBRs[7]. In this study, we focused on extracellular proteins secreted in pilot-scale MBRs as an effective fouling indicator, and investigated the shifts in their concentrations throughout the operational period. Based on the relationships among the extracellular protein concentration, TMP, flux, and chemical oxygen demand (COD), we propose a preliminary diagnostic method for membrane fouling prior to the increase in TMP.

2. Materials and Methods

Schematic configuration of the pilot-scale MBR used in this study is shown in Fig. 1. The reactor has three compartments with operating volumes of 92.0, 80.5, and 57.5 l (from left to right compartments in Fig. 1). A 0.24-m^2 flat polyacrylonitrile membrane module (M-fine; Awa Paper Mfg, Co., Tokushima, Japan) with 0.07 μm pore size was fixed in the rightmost compartment. The membrane module was operated with the cycle of a permeate extraction for 9 min and a pause for 1 min. Air was provided through an air diffuser set in each compartment at a flow rate ranging from 12.5 to 40.0 l min^{-1} for mixing the activated sludge and for controlling

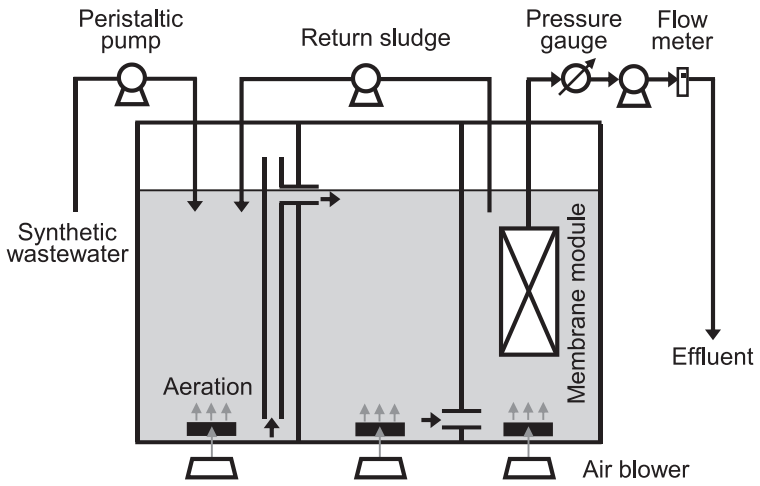

Fig. 1. Schematic of the configuration of the pilot-scale MBR.
The total volume of the pilot-scale MBR was 230 l. The flow rates of influent synthetic wastewater, return sludge, and effluent were 115 l day^{-1} (hydraulic retention time=2 days). The activated sludge was continuously aerated.

dissolved oxygen levels. The submerged membrane surface was also aerated continuously to reduce membrane fouling. The employed activated sludge was obtained from a municipal wastewater treatment plant (Kinu aqua-station, Ibaraki, Japan). Throughout the experimental period, the bioreactor was constantly fed with a synthetic wastewater stored in a 20-l feed tank at 4°C. The flow rate of both the input wastewater and the output membrane-filtered treated water was 115 l day^{-1}, resulting to a hydraulic retention time of 2 days. The flow of the return sludge from rightmost to leftmost compartments was also set at 115 l day^{-1}, and no sludge was withdrawn from the reactor except for sampling. The organic concentration of the original synthetic wastewater was set at 450 mg-COD l^{-1} and the wastewater contained (g l^{-1}): CH_3COONa, 2.65; NH_4Cl, 0.376; KH_2PO_4, 0.109; peptone, 0.706; as well as trace elements (mg l^{-1}): $FeCl_3 \cdot 6H_2O$, 0.782; $CaCl_2$, 1.56; $MgSO_4$, 1.56; KCl, 1.56; NaCl, 1.56.

Two pilot-scale MBRs were operated independently, and both run were subjected to the low organic-loading-rate (OLR) operation with the wastewater of 450 mg-COD l^{-1} described above, followed by the high OLR operation with the wastewater of 900 mg-COD l^{-1} in order to promote membrane fouling.

(i) Run 1: The MBR was operated for 46 days under constant flow rates for input and output mentioned above. A part of the operation data was already published in our previous report[10]. The organic concentration in the influent was initially adjusted to 450 mg-COD l^{-1}, and on day 22 of the operation, the substrate concentration was doubled, increasing COD from 450 to 900 mg l^{-1}.

(ii) Run 2: The MBR was operated for 33 days the same conditions of Run 1. The operation data was partially published in our previous reports[9,11]. The COD in the influent was initially adjusted to 450 mg l^{-1}, and on day 8 of the operation, the concentration was increased to 900 mg l^{-1}.

In both runs, sludge samples were taken from the second compartment of the MBRs. The solid constituent of each activated sludge sample (15 mL) was separated by centrifugation (15,300×*g*, 15 min, 4°C) and removed. The resulting supernatant was further filtered by using a cellulose acetate membrane (*Φ*, 0.20 μm, C020A025A; ADVANTEC, Tokyo, Japan), and it was stored at 4°C until use. The concentration of extracellular proteins in the supernatant was determined by using Quick Start Bradford protein assay reagent (Bio-Rad, Hercules, CA, USA). The COD-Mn value in the effluent was determined by permanganate titration according to the method defined in Japanese standards for water effluent. The TMP of membrane module and the effluent flow rate were monitored during the operation of the MBRs.

3. Results and discussion

(i) Run 1: Changes in the protein concentration, TMP of the membrane module, effluent flow rate, and effluent COD-Mn level during MBR operation are shown in Fig. 2. Throughout the 46 days of operation, the COD-Mn levels in the effluent gradually increased but only to levels below the Japanese effluent standard of 160 mg-COD-Mn l^{-1} (Fig. 2D). In contrast, the protein concentration rapidly increased from 4.5 mg l^{-1} at day 11 to 47 mg l^{-1} at day 15 (arrow I in Fig. 2A). Although the protein concentration decreased to 10–20 mg l^{-1} during days 23–24, it again increased to approximately 70 mg l^{-1} after day 35 (Fig. 2A).

Ten days after the first increase in protein concentration (arrow II in Fig. 2B), the TMP began to increase. After another 11 days (arrow III in Fig. 2C), the effluent flow rate started to decrease, indicating the initiation of membrane fouling.

(ii) Run 2: Changes in the physicochemical parameters are shown in Fig. 3. The COD-Mn value in the effluent also increased gradually, but remained below 160 mg l^{-1} throughout the 33 days of operation (Fig. 3D). The protein concentration increased suddenly to 42.5 mg l^{-1} at day 15 (arrow I in Fig. 3A), subsequently decreased to 20–30 mg l^{-1}

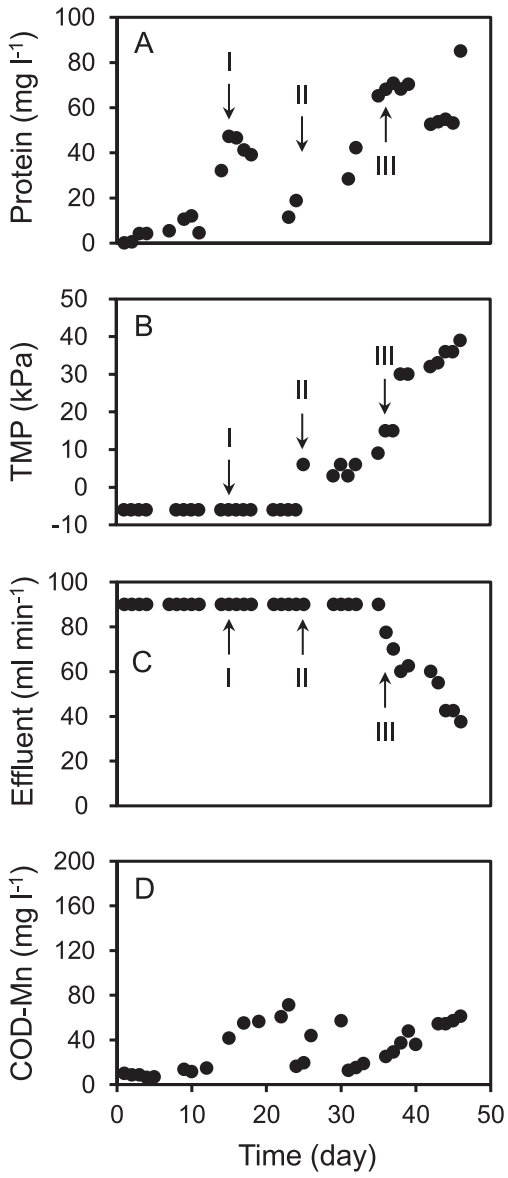

Fig. 2. Changes in physicochemical parameters of the pilot-scale MBR during Run 1.
Protein concentration in the sludge (A), TMP of the membrane module (B), effluent flow rate (C), and COD-Mn in the effluent (D). The Roman numerals indicate the start points of protein concentration increase (I), TMP increase (II), and effluent flow rate decrease (III).

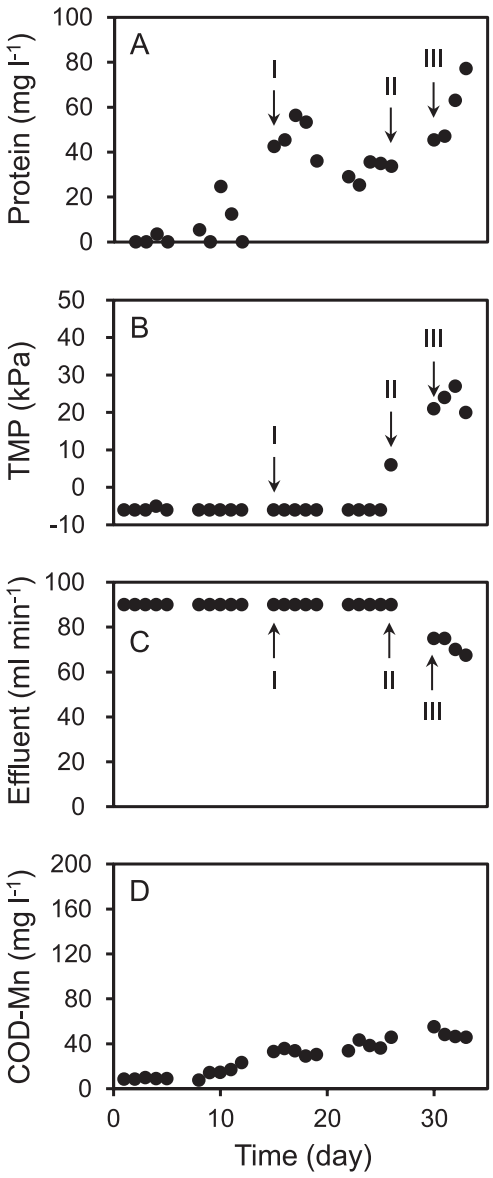

Fig. 3. Changes in physicochemical parameters of the pilot-scale MBR during Run 2.
Protein concentration in the sludge (A), TMP of the membrane module (B), effluent flow rate (C), and COD-Mn in the effluent (D). The Roman numerals indicate the start points of protein concentration increase (I), TMP increase (II), and effluent flow rate decrease (III).

during days 22–23, and exhibited a second increase to 60–80 mg l^{-1} after day 31 (arrow III in Fig. 3A). These findings are very similar to those of Run 1. Run 2 also mirrored the findings of Run 1 in this experimental conditions that the TMP began to increase 11 days after the first increase in the protein concentration (arrow II in Fig. 3B), and that the effluent flow rate decreased 4 days afterward (arrow III in Fig. 2C).

The results obtained from two different MBR operations showed that the first significant increase in the extracellular protein concentration occurred before membrane fouling was detected by the TMP increase and the flux decrease. This implied that the initial accumulation of extracellular proteins at a level above 40 mg l^{-1} is a potential predictive indicator of membrane fouling that emerges before the TMP can be used as an indicator.

In contrast, in another period of stable MBR operation for 109 days, which was conducted only under low OLR conditions (COD in the influent: 450 mg l^{-1}), the protein concentration, TMP, and COD-Mn in the effluent all remained stable throughout the operational period (data not shown), implying that membrane fouling had still not reached a severe stage within this period.

Considering that a filtration membrane can be fouled even

if the concentrations of organic substances in the effluent do not exceed the Japanese effluent standard value [COD-Mn (160 mg l^{-1})], measurements of organic substance concentration were not useful as fouling indicators. However, increasing protein concentrations were observed before the increase in TMP during membrane fouling in this experimental conditions, suggesting that the detection of an initial increase in protein concentration to above 40 mg l^{-1} can be a preliminary diagnostic method for membrane fouling.

4. Conclusion

In the pilot-scale MBR, we established a preliminary diagnostic method for membrane fouling using extracellular proteins. An initial increase in the protein concentration to above 40 mg l^{-1} can be a predictor of a TMP increase approximately 10 days later. Since the protein concentration is easily determined by a standard protocol, this method may be used on site. To enable the practical use of this method, further studies investigating different situations, such as different solid retention times and different types of wastewater, are necessary.

Acknowledgments

We would like to acknowledge the Kinu-aqua station for kindly providing the activated sludge. We thank Mr. Takayuki Iijima, Ms. Maki Yanagisawa and Ms. Yumiko Kayashima (National Institute of Advanced Industrial Science and Technology) for operating the reactor and analyzing water samples.

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