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Application of glyco-blotting for identification of structures of polysaccharides causing membrane fouling in a pilot-scale membrane bioreactor treating municipal wastewater

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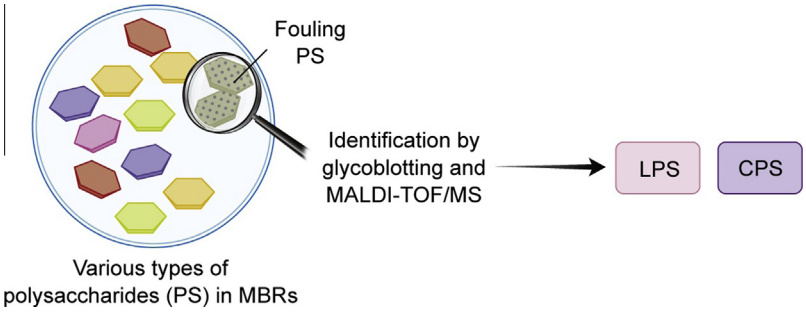
HIGHLIGHTS

- A new approach for the analysis of polysaccharides in wastewater systems is proposed.
- Fairly clear MS spectra could be obtained for polysaccharides in an MBR.
- Structures and origins of polysaccharides were postulated based on MS spectra.
- Major polysaccharides in the foulants were not dominant in the supernatant.
- CPS and/or LPS seemed to be key players in the evolution of membrane fouling in MBRs.

GRAPHICAL ABSTRACT



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ABSTRACTS

A new approach for the analysis of polysaccharides in membrane bioreactor (MBR) is proposed in this study. Enrichment of polysaccharides by glyco-blotting, in which polysaccharides are specifically collected via interactions between the aldehydes in the polysaccharides and aminooxy groups on glycoblotting beads, enabled MALDI-TOF/MS analysis at a high resolution. Structures of polysaccharides extracted from fouled membranes used in a pilot-scale MBR treating municipal wastewater and those in the supernatant of the mixed liquor suspension in the MBR were investigated. It was found that the overlap between polysaccharides found in the supernatants and those extracted from the fouled membrane was rather limited, suggesting that polysaccharides that dominate in supernatants may not be important in membrane fouling in MBRs. Analysis using a bacterial carbohydrate database suggested that capsular polysaccharides (CPS) and/or lipo-polysaccharides (LPS) produced by gram-negative bacteria are key players in the evolution of membrane fouling in MBRs.

1. Introduction

Membrane bioreactors (MBRs) are promising technologies for future municipal wastewater treatment due to their high

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performance and their suitability for satellite/decentralized systems (Asano et al., 2006). However, membrane fouling, which results in the decline of membrane permeability in long-term operations, remains a major concern. Many attempts have been made to control membrane fouling in MBRs, none of which have turned out to be very effective (Malaeb et al., 2013). Because of this, MBRs are still not a mainstream technology in municipal wastewater treatment.

Detailed information on foulants is indispensable for the effective control of membrane fouling in MBRs. The consensus is that the soluble and colloidal fractions of the mixed liquor suspension in MBRs play an important role in the development of membrane fouling (Defrance et al., 2000; Bouhabila et al., 2001; Yamato et al., 2006; Fan et al., 2006; Teychene et al., 2008). In particular, the involvement of polysaccharides in membrane fouling in MBRs has been reported (Kimura et al., 2005; Rosenberger et al., 2006). In previous studies where ^{13}C NMR analysis was carried out for foulants extracted from MBRs, it was shown that polysaccharides were quantitatively dominant in the foulants (Kimura et al., 2005, 2008). In the majority of the relevant studies, polysaccharides were measured by colorimetric methods such as the phenol sulfuric acid method (Dubois et al., 1956) as a sum parameter. However, such methods might not be informative enough to predict the operational performance of MBRs (Al-Halbouni et al., 2009; Kimura et al., 2009). Rather, it should be considered strange if a sum parameter of polysaccharides can describe membrane fouling in MBRs, considering the fact that polysaccharides in the mixed liquor suspension of an MBR are not at all uniform: a tremendous diversity of polysaccharides in the suspension is expected, although such diversity has not been yet revealed. The authors have shown that characteristics of foulants in MBRs vary depending on operational parameters such as F/M ratio, membrane flux, membrane materials, cross-flow conditions and temperature (Kimura et al., 2005, 2008; Yamato et al., 2006; Miyoshi et al., 2009; Hoque et al., 2012). To a certain extent, this reflects the diversity of polysaccharides in MBRs. It is therefore interesting to determine the structures of the polysaccharides that are important in the development of membrane fouling in MBRs.

A previous study partially revealed the diversity of polysaccharides in MBRs by using lectin-affinity chromatography (Kimura et al., 2012), demonstrating the presence of polysaccharides with high fouling potentials. In the same study, structures and origins of polysaccharides with high fouling potentials were suggested on the basis of MALDI-TOF/MS analysis. In the trial MS analysis, however, the quality of the MS spectra was not high, likely due to insufficient purification of the samples. As a result, the information on the structures and origins of polysaccharides obtained in that study was limited and biased by many factors.

Knowledge of the diversity of the polysaccharides in MBRs is still quite limited, and it is therefore difficult to establish effective methods for controlling membrane fouling in MBRs. Increasing the amount of basic information available is crucial. Recently, the "glycoblotting method", a practical and highly sensitive method for oligosaccharides enrichment, was developed and can be used for the analysis of biological samples such as sera, cells, and egg whites (Kita et al., 2007; Miura et al., 2008, 2010; Furukawa et al., 2008; Amano et al., 2010). In this method, oligosaccharides are selectively captured by selective chemical ligation between the aldehyde group at the reducing terminus of the oligosaccharide and an aminooxy group displayed on glycoblotting beads, followed by labeling the molecules to increase sensitivities in the subsequent MALDI-TOF/MS analysis.

The present study applies the glyco-blotting method to the oligosaccharides obtained by the partial hydrolysis of polysaccharides that cause membrane fouling in a pilot-scale MBR. Further examination of the structures and origins of polysaccharides that cause membrane fouling in the MBR were carried out. This study describes the first trial that applies the enrichment method to wastewater polysaccharides that display extreme heterogeneity. Due to the effectiveness and high efficiency of the method, as demonstrated, structures of polysaccharides that caused membrane fouling in the MBR could be suggested with a high degree of accuracy.

2. Methods

2.1. Sample collection

All samples were obtained from the pilot-scale MBR installed at the Soseigawa Wastewater Treatment Plant (Sapporo, Japan), which is described in detail elsewhere (Kimura et al., 2005, 2008; Hoque et al., 2012). Wastewater examined in this study was classified as "weak": average total organic carbon (TOC) concentration and total nitrogen (T-N) concentration during the experiments were 40.6 mg/L and 26.7 mg/L, respectively. During the sampling periods, the sludge retention time was set at 30 days. The mixed liquor suspended solids (MLSS) concentration in the biological tank was 12 g/L on average. The pilot-scale MBR used in this study was a side-stream type equipped with tubular membranes made from PVDF polymer. The nominal pore size of the membrane was 0.05 μm.

Extraction of foulants from the fouled membranes was performed three times in May–August in 2011. The three samples are designated foulant 1, 2 and 3 hereafter. Before the sampling campaign, the MBR had been operated for >3 months under the same conditions as those used in this study. Therefore, sufficient acclimatization of biomass in the reactor could be assumed. After operating for 10–20 days with a membrane flux of 42 LMH, the membrane module was disconnected from the system and was subject to foulant extraction. New membranes were used in each experiment.

Supernatants of the mixed liquor suspension of the MBR (supernatants 1–3) were also collected a few days before the membranes were disassembled for foulant extraction (i.e., foulants 1–3).

2.2. Extraction of foulants

Prior to foulant extraction, membrane modules were disassembled. Each membrane tube was opened by using a stainless cutter knife, and the surface of active layer was gently wiped with a sponge. This was carried out to eliminate bias caused by the cake on the membrane surface and to focus on irreversible fouling, which is important to be controlled (Kimura et al., 2004, 2005). Macroscopic deposition of particles on the membrane surface (i.e., formation of cake layer) can be avoided by implementing efficient physical cleaning such as intensive backwashing or the introduction of granular materials (Siembida et al., 2010). As for the present operations, it was confirmed that the contribution of the cake to the total filtration resistance was minor in the MBR, thanks to the effective physical cleaning of the membrane provided by two-phase flow (Hoque et al., 2012). However, sponge cleaning was carried out in this study to assure that foulants causing irreversible fouling were investigated. Wiped membrane specimens were then immersed in an alkaline solution (NaOH, pH 12) for 24 h at 25 °C to obtain foulants 1–3. Concentrations of polysaccharides in foulants 1–3 were assessed by the phenol sulfuric acid method. The concentrations of polysaccharides in foulant 1, 2 and 3 were 23.6, 6.1 and 23.6 mg/L, respectively. Extracted foulants were then partially hydrolyzed by hydrochloric acid (Kimura et al., 2012) to obtain oligosaccharides for subsequent MS analysis. Hydrolyzed samples were kept in a freezer until the next step.