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Characterization of the size-fractionated biomacromolecules: Tracking their role and fate in a membrane bioreactor

Fangang Meng [a,*], *Zhongbo Zhou* [a], *Bing-Jie Ni* [b], *Xing Zheng* [c], *Guocheng Huang* [a], *Xiaoshan Jia* [a], *Shiyu Li* [a], *Ya Xiong* [a], *Matthias Kraume* [d]

[a] *School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, PR China*
[b] *Department of Environmental Engineering, Technical University of Denmark, Miljøvej Building 113, 2800 Kongens Lyngby, Denmark*
[c] *Department of Water Quality Control, Technische Universität Berlin, Sekr. KF4, Straße des 17, Juni 135, 10623 Berlin, Germany*
[d] *Chair of Chemical and Process Engineering, Technische Universität Berlin, Str. des 17. Juni 135, MA 5-7, 10623 Berlin, Germany*

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ABSTRACT

This article presents a study aimed at the fractionation and characterization of what is thought to be one of the most complex organic mixtures produced by activated sludge: biomacromolecules (BMM). Photometric quantification combined with excitation–emission matrix (EEM) fluorescence spectroscopy and nuclear magnetic resonance (NMR) measurements were used to characterize BMM in a membrane bioreactor (MBR) from a chemical perspective. Overall, the BMM in sludge supernatant were mainly present in three fractions: colloidal BMM (BMM_c, >0.45 μm), biopolymeric BMM (BMM_b, 0.45 μm–100 kDa) and low molecular weight (MW) fraction (<5 kDa). The analysis of fluorescence regional integration (FRI) showed that the organics in membrane permeate and those in the low-MW fraction of sludge supernatant were of similar chemical composition. The characterization by NMR suggested that the BMM_c fraction had similar carbon content of proteins and polysaccharides. In contrast, the BMM_b and the low-MW BMM were proved to be carbonaceous and aromatics, respectively. Moreover, because of the high MW and gelling property, polysaccharides were found to have a high potential to accumulate on the membranes. In addition, the lipids present in the BMM_b of the sludge supernatant were demonstrated to be another important foulant due to their large size. Our results also indicated that aromatic proteins had a higher fouling propensity than tryptophan proteins though they were of similar size nature. This work could be useful for better understanding of the chemical nature of BMMs in MBRs.

1. Introduction

Biomacromolecules (BMM) are a pool of complex mixture produced by microorganisms as a result of substrate metabolism and biomass growth/decay during biological wastewater treatment (Laspidou and Rittmann, 2002; Ni et al., 2010). The major chemical constituents of BMM are proteins, polysaccharides, humic substances, low molecular weight organic acids, etc. The generation and presence of BMM in wastewater treatment systems are one of the major reasons determining the quality of the treated water. In particular, BMM are believed to the primary compounds leading to membrane fouling in membrane-based technologies used for water and wastewater treatments such as membrane bioreactors (MBRs)

* *Corresponding author*. Tel.: +86 20 39335060.
E-mail address: fgmeng80@126.com (F. Meng).
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(Huang et al., 2000; Fan et al., 2006; Jarusutthirak and Amy, 2006; Ramesh et al., 2007). In MBRs, the BMM compounds larger than membrane pore size can be rejected, in which biodegradable BMM can be used as substrates for microorganisms, and the small-size ones can be discharged along with membrane permeate (Song et al., 2007; Meng et al., 2009a). Finally, the refractory and large-size BMM compounds are accumulated in the bioreactor or on membranes.

Considering the significance of BMM in MBRs, numerous research efforts have been made in recent years (Meng et al., 2009b; Drews, 2010). The fouling propensity of BMM strongly depended on their size (Laabs et al., 2006; Rosenberger et al., 2006), composition (Chen et al., 2006; Rosenberger et al., 2006; Drews et al., 2008; Ng et al., 2006; Ng and Ng, 2010), and hydrophobic/hydrophilic nature (Liang et al., 2007; Yamamura et al., 2008; Tian et al., 2009). For instance, the hydrophilic substances with a molecular size above approx. 120 kDa, called biopolymers, were found to be the predominant foulants in MBRs (Rosenberger et al., 2006). Similarly, Liang et al. (2007) also showed that hydrophilic neutrals (e.g., polysaccharides) were likely responsible for the high fouling potential of BMM. Using a field flow fractionation (FFF), it was found that the lower molar-mass compounds in bacterial extracellular polymeric substances was dominated by protein-like substances, whereas the higher molar-mass fraction was rich in exoproteins and exopolysaccharides (Alasonati and Slaveykova, 2011). Based on the fractionation with centrifugation, Teychene et al. (2008) found that the MBR fouling is mainly governed by soluble BMM rather than colloidal fraction. Nonetheless, opposite conclusions were drawn as well. Lee et al. (2003), for example, reported that the hydrophobic proteins played an important role in membrane fouling due to their hydrophobic interactions with membranes. Indeed, hydrophobic and rough membranes have higher potential to be fouled by BMM than hydrophilic and smooth ones (Zhang et al., 2008). Such contradictions in previous research efforts are mostly due to the poor understanding of BMM, e.g., the BMM in previous studies may have different chemical or structural composition. In order to better understand the membrane fouling in MBRs, it is essential to characterize the BMM more comprehensively.

In fact, a number of characterization methods focussing on component or size fractionation have been used in numerous studies (Leenheer, 1981; Liang et al., 2007). For example, XAD resin was used to separate the BMM into hydrophobic, hydrophilic, and transphilic constituents (Leenheer, 1981), which can aid in understanding the BMM in terms of hydrophobic/hydrophilic nature. Using a field flow fractionation (FFF), it was found that the lower molar-mass compounds in bacterial extracellular polymeric substances was dominated by protein-like substances, whereas the higher molar-mass fraction was rich in exoproteins and exopolysaccharides (Alasonati and Slaveykova, 2011). Based on the fractionation with centrifugation, Teychene et al. (2008) found that the MBR fouling is mainly governed by soluble BMM rather than colloidal fraction. In addition, the BMM can also be fractionated by filtering the samples through a series of membranes with different molecular weight cut-offs (MWCOs). Unfortunately, the characterization of the size-fractionated BMM was currently limited to the quantification of dissolved organic carbon (DOC) (Liang et al., 2007), which can only provide rough information about the chemical nature of BMM. Indeed, a detailed characterization of the size-fractionated BMM can lead to a deeper understanding on BMM compounds, which can hopefully clear up the misunderstanding dealing with the contradictions in previous studies. More importantly, it is of high interest to track the origins of membrane foulants and the fate of BMM in the MBR process by an in-depth characterization of BMM. To date, however, only a few investigations have been conducted to identify the true chemical composition of the size-fractionated BMM.

The objective of this study, therefore, was to characterize the individual chemical components of the size-fractionated BMM in order to better understand the membrane fouling in MBRs. The size fractionation was achieved by filtering samples with a series of membranes with different MWCOs. Different BMM components were identified and quantified using photometric methods. Furthermore, excitation-emission matrix (EEM) fluorescence spectroscopy and ^{13}C nuclear magnetic resonance (NMR) were used to reveal the chemical/structure nature of these BMM components.

2. Materials and methods

2.1. The MBR setup

A lab-scale MBR with an effective volume of 50 L was used in this work, which consisted of anoxic, aerobic, anoxic, anaerobic, and membrane tank (see Fig. S1 of Supporting Materials (SM)). The MBR was designed for simultaneous removal of organic carbon, nitrogen and phosphorous. A 0.23 m^2 flat-sheet membrane module (PVDF, 0.1 μm, Sinap Corp., Shanghai, China) was submerged in the membrane tank. This membrane is commercially used for industrial and municipal wastewater treatments particularly in China. The membrane module was constantly sucked with a peristaltic pump, and physical or chemical backwashing was not performed. As the transmembrane pressure (TMP) reached 0.025 MPa, the membrane module was washed with high pressure water and then was soaked in 0.3% NaClO solution for about 12 h. A complex synthetic wastewater simulating municipal wastewater was used as feedwater (see Table S1 of SM). The COD, TN, and TP in the feedwater were in the range of 310–400, 62–81, and 8–15 mg/L, respectively. Hydraulic retention time (HRT) and solid retention time (SRT) were set at 12–14 h and 20 days, respectively. Concentrations of the mixed liquid suspended solids (MLSS) in the membrane tank were in a range of 6000–7000 mg/L. Weekly, the BMM of feedwater, sludge supernatant and membrane permeate were sampled and measured.

2.2. Sampling of membrane foulants

Due to the fact that the use of chemicals such as acids or alkaline solution may damage the original composition of membrane foulants, the membrane foulants were obtained by washing the fouled membrane module with high pressure water. Thus, only the removable compounds on the fouled membranes were obtained and analyzed. In fact, the foulants