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Membrane fouling in a membrane bioreactor: High filtration resistance of gel layer and its underlying mechanism

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ABSTRACT

A membrane bioreactor (MBR) was continuously operated to investigate mechanisms of fouling caused by the gel layer in this study. Agar was used as a model foulant for gel layer formation, and filtration resistance of gel layers was systematically assessed. The results showed that gel layer possessed unusually high specific filtration resistance (SFR) and high measured porosity as compared with cake layer. Current knowledge cannot explain the contradiction between high filtration resistance and high porosity of gel layer. A new fouling mechanism based on Flory-Huggins theory was then proposed. Filtration resistance of agar gel layer was found to be independent of pH and ionic strength, but linearly increase with gel thickness. The results are accordant with the mechanism deductions. Simulation of the mechanism model showed that the filtration resistance induced by mixing chemical potential variation was comparable to the experimental data of filtration resistance of agar gel layer, indicating that the proposed mechanism is the predominant mechanism responsible for the high filtration resistance of gel layer. The proposed mechanism was further verified from the bound water viewpoint.

1. Introduction

Membrane filtration processes have attracted increasing interest due to their potential applications and advantages. However, membrane fouling is inevitable and considered as the primary limitation in their real applications (Drews, 2010; Lin et al., 2014; Loulergue et al., 2014).

Membrane fouling in wastewater treatment processes like membrane bioreactor (MBR) system can be generally characterized as initial pore clogging followed by foulant layer formation (Meng et al., 2009a; Lin et al., 2014). Foulant layer can be further distinguished as gel layer and cake layer. It was reported that gel layer was formed from the gelation of the colloidal and dissolved matters (note that these matters were termed as "gelling foulants" in this study) (Rosenberger et al., 2006; Wang and Waite, 2009; Yang et al., 2011; Xiao et al., 2013), and in lots of cases, the gelling foulants were the main contributors of membrane fouling (Wang and Waite, 2008a, 2008b; Yang et al., 2011). Under similar conditions, it was reported that the specific filtration resistance (SFR) of gel layer was almost 100 times higher than that of cake layer (Hong et al., 2014). In other side, the gel layer formed in MBRs is generally thin and porous (Wang and Waite, 2008a, 2008b; Hong et al., 2014). For model gel layers, Yarnpakdee et al. (2015) observed that *Gracilaria* agar gel had coarse network with the large voids. Xin et al. (2015) found that Ca-alginate gel layer displays a distinct "honeycomb" structure with high porosity. Harnkarnsujarit et al. (2012) reported that the freeze-dried agar gel had extremely high porosity. According to Carman Kozeny equation (Bai and Leow, 2002), thin and high porous layer corresponds to low filtration resistance. There apparent exists a contradiction among the literature results. This contradiction has been frequently pointed out by some previous studies (Wang and Waite, 2008b, 2009; Hong et al., 2014). Exploring the underlying causes of this contradiction has drawn significant attention. It was suggested that multivalent cation complexation was principally responsible for the high SFR of gel layer (Wang and Waite, 2009). However, as gel layer formation can be independent of multivalent cation complexation, this mechanism was not likely the exact causes. Recently, Hong et al. (2014)

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proposed a new mechanism, namely osmotic pressure-induced resistance, which was considered as the main contributor of the SFR of gel layer. The osmotic pressure-induced resistance was proposed to be generated from the chemical potential difference between permeate and foulant layer carrying abundant negatively charged functional groups (Zhang et al., 2013). Considering that the main component implicit in gel formation in MBRs has been identified to be the polysaccharides which can be almost electroneutrality, this mechanism can neither be regarded as the exact cause. It can be concluded from literature studies that the exact causes of high SFR of gel layer remained unrevealed. Nevertheless, above mentioned study introduced "chemical potential" conception into membrane fouling research (Hong et al., 2014), and did provide important hints to further explore the underlying mechanisms of gel layer fouling. As all the organic macromolecules prevailing in MBRs regardless of proteins and polysaccharides have somewhat gelling propensity (Wang and Waite, 2008b), it is of universal significance to reveal the exact mechanisms of high filtration resistance of gel layer for membrane fouling mitigation.

Sodium alginate and agar are two typical model substances for gel layer formation. Sodium alginate is high negatively charged, and involves the effects of negatively charged functional groups and multivalent cation complexation when it used to form gel layer. In this study, in order to exclude these effects, agar was selected as a model foulant to simulate gel layer in a MBR. The formed gel layer was characterized, and its filtration resistance under different conditions was systematically assessed. Based on these data, the underlying mechanism was proposed and verified.

2. Material and methods

2.1. Experimental setup and operation

A lab-scale submerged MBR (SMBR) setup with 65 L effective volume (dimension of 0.54 × 0.30 × 0.40 m height × length × width) as shown in Fig. 1 was continuously operated for more than 400 days. The flat sheet membrane model consisting of five flat-sheet membrane elements was used in the SMBR, which was supplied by Shanghai SINAP Co. Ltd. The membrane was made from polyvinylidene fluoride (PVDF) with a normalized pore size of 0.1 μm. Membrane flux during the operational period was maintained approximately 30 L m^{-2} h^{-1} (LMH). The operational details can refer to Zhang et al. (2013).

2.2. Analytical methods

Gel layer formation occurred during start-up period of SMBR operation. The real gel layer samples were obtained by scraping off gel layer on membrane surface. The content of polysaccharides and proteins in real gel samples was colorimetrically measured by phenol/sulfuric acid method (DuBois et al., 1956) and Folin method (Lowry et al., 1951), respectively. Agar was used as a model of the polysaccharides for gel layer formation. The agar gel was prepared as follows: Agar solution samples with different concentration were prepared by adding specific amount of agar powder into the ultrapure water, and thereafter, the agar mixtures were dissolved by heating in a microwave oven for 11 min. The solution was cooled to 35 °C, and then was placed in an electric-heated thermostatic water to maintain the solution temperature at 35 °C. The sludge suspension samples were obtained directly from the stable operation MBR reactor. These samples were then utilized for the following analyses.

Zeta potential of agar sample was measured by using a Zetasizer Nano ZS electrophoretic light scattering spectrophotometer based on laser Doppler electrophoresis technique. The background electrolyte was adjusted to 0.01 mol L^{-1} NaCl solution by adding corresponding amount of NaCl particles in the preparation of agar solution. Structure of the cake layer and gel layers was analyzed by a scanning electron microscopy (SEM). In order to obtain SEM images, the samples were freeze-dried in a freeze-dryer (Labconco Freezone 12, USA) at −35 °C for 5 days (until freeze-dried). The SEM images were acquired and transferred to gray-scale formation (256 gray-scale levels) with Adobe Photoshop CS3 software. The resulted images were then transformed to binary images by selecting a threshold. The pore area values can be determined by analyzing the binary images. Triplicated measurements were performed and the

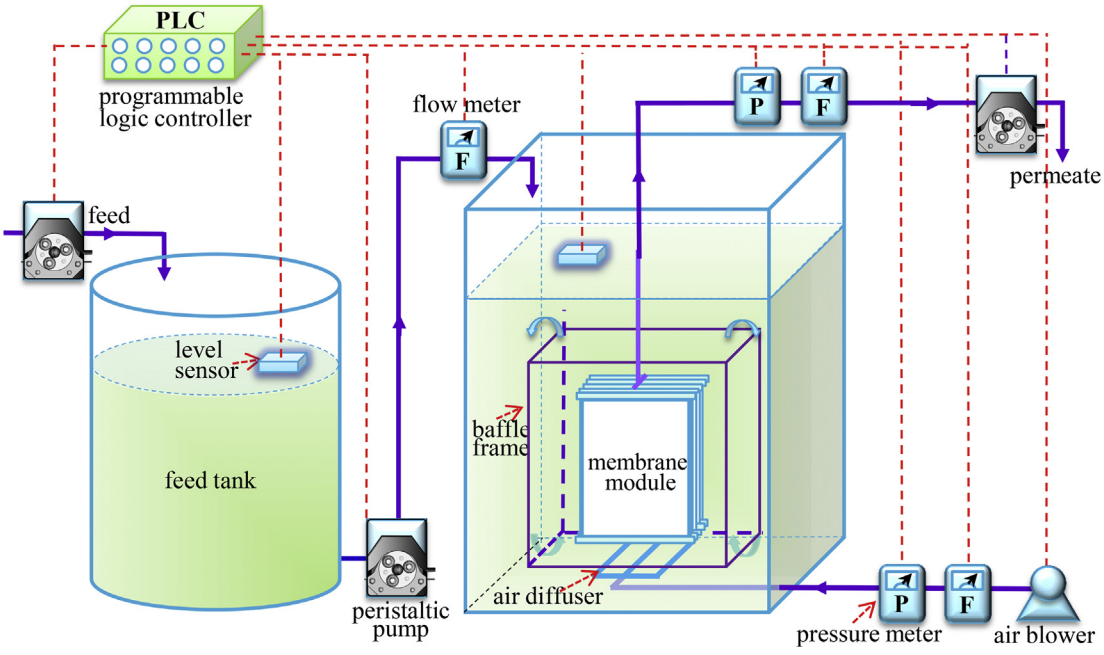

Fig. 1. Schematic of the lab-scale SMBR system.