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Membrane fouling in a membrane bioreactor: A novel method for membrane surface morphology construction and its application in interaction energy assessment

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ABSTRACT

A novel method was developed to construct membrane surface morphology in this study. The method was based on fractal geometry theory, and involved a modified Weierstrass-Mandelbrot (WM) function for modeling surface topography. With MATLAB programming, membrane surface could be graphically modeled. It was found that the fractal dimension (D_f) and cutoff frequency (L_s) were the two key parameters affecting the topography, and the membrane surface constructed by this method could be very close to the real situation. The method was then applied in interaction energy assessment regarding membrane fouling in a membrane bioreactor. The procedure which combines membrane surface topography construction, surface element integration (SEI) method and the composite Simpson's rule was theoretically proposed. The surface properties of foulant and membrane were experimentally measured. Accordingly, a membrane surface was reconstructed for interaction energy assessment. With these data, quantitatively assessing interfacial interactions between foulant particles and a nearly-real rough membrane surface is expected to be firstly realized. This study provided a complete solution for quantitative assessment of interaction energies between a foulant particle and rough membrane surface.

1. Introduction

Membrane bioreactor (MBR) which integrates membrane filtration units into biological processes for wastewater treatment features lots of advantages, such as higher organic removal efficiency, reduced footprint and sludge production, and easy manipulation as compared with conventional activated sludge systems [1–3]. Membrane fouling, however, remains the primary bottleneck for the wide application of MBR technology [1,4,5]. Therefore, considerable interest has been focused on membrane fouling research. Membrane fouling is resulted from interactions between foulants and membrane. Adhesive membrane fouling, a major fouling form in MBRs, is considered to be directly determined by the interfacial interactions between foulants and membrane [4–7]. Accurate knowledge of the interfacial interactions is of essential importance for understanding of adhesive membrane fouling and its control.

Interfacial interactions between two surfaces can be generally described using the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory, which combines three kinds of interactions: Lifshitz-van der Waals (LW), electrostatic double layer (EL), and acid-base (AB) interaction energies [8]. While XDLVO theory is only applicable to interfacial interactions between two smooth flat surfaces [8], real interaction scenarios involve morphological heterogeneity of both membrane and foulant surface. Particularly, atomic force microcopy (AFM) scans have confirmed that almost all of the commercial membranes prevailed in MBR applications had complicated surface morphology [9–11]. Lots of studies reported that membrane fouling was significantly affected by membrane surface morphology [9,12–15]. This situation gave remarkable impetus to the development of surface element integration (SEI) method [16,17], which integrates the interaction energy per unit area between opposing differential planar elements over the entire surfaces, theoretically allowing to quantitatively calculate the interaction energy taking into account the surface morphology. This means that interfacial interactions are directly dependent of membrane surface morphology. Although

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membrane fouling and interfacial interactions have been extensively studied [1,4,7], the associated issue, construction of membrane rough surface morphology, which could be of great interest in membrane fouling, has received little progress.

Membrane surface morphology is traditionally considered to be a stationary random process [18,19]. In light of this knowledge, a common approach to construct solid substance surface involves random placement of geometrically regular asperities as protrusions or depressions on a smooth surface [20]. Asperities of various regular shapes, including hemispheres [21], cylinders [22] and cones [23], have been adopted in literature. However, the reconstructed surface by this approach appears too regular, and significantly differs from the real surfaces of natural subjects. Another common approach to construct solid substance surface is describing surface morphology by periodic or random functions, such as the sine function [24] or Gaussian function [25]. Albeit advantageous compared with the first common approach, this approach also fails to mimic the actual natural membrane surface morphology to a large extent. Different from intuition, experiments have shown that the surface morphology is of nonstationary process, and the corrugation of the surface height might contain a broad bandwidth [26]. Moreover, natural solid surfaces including membrane surfaces generally contain typical fractal characteristic, Jaggard and Sun [27] introduced the fractal geometry into the study of rough surface. The fractal geometry serves as a bridge between a periodic function and a random function, and thus leads to significant insights into construction of surface morphology. As the fractal geometry could combine short-range disorder with long-range order as the features of rough surfaces [28], the constructed surface could be much close to the real surface. Thielen et al. [29] found that the function based on fractal geometry would well describe and characterize turned shaft surfaces. Despite the potential advantages of fractal geometry, to our knowledge, no one used this conception in construction of membrane surface morphology for membrane fouling study. Moreover, the interfacial interactions between foulants and constructed rough membrane surface remain unexplored.

The objective of this study was, therefore, to develop a new method for constructing membrane surface topography, and to assess the interfacial interactions between foulants and the constructed membrane surface in an MBR system. The surface properties of both membrane and foulant samples were experimentally measured. Weierstrass-Mandelbrot (WM) function involving the fractal geometry was adopted in construction of membrane surface morphology. The constructed morphology together with composite Simpson's rule was then included in SEI method for assessment of interfacial interactions. This study would provide a primary approach for constructing membrane surface topography.

2. Material and methods

2.1. MBR system

A submerged MBR system with dimension of $0.54 \times 0.30 \times 0.40$ m height × length × width was operated for over 300 days. The simulated municipal wastewater with the composition of 300 mg COD/L glucose plus the mineral medium was used as influent. The mineral medium had composition as follows: Na_2CO_3 (46 mg Na/L); $NaHCO_3$ (23 mg Na/L); $(NH_4)_2SO_4$ (27 mg N/L); KH_2PO_4 (7 mg P/L); $MgSO_4$ (7 mg Mg/L); $CaCl_2$ (6 mg Ca/L); $FeCl_3$ (4 mg Fe/L); $ZnCl_2$ (0.11 mg Zn/L); $CoCl_2$ (0.1 mg Co/L); $NaMoO_4$ (0.07 mg Mo/L); $MnSO_4$ (0.04 mg Mn/L) and $CuSO_4$ (0.03 mg Cu/L). The polyvinylidene fluoride (PVDF) membrane purchased from Shanghai SINAP Co. Ltd. was used as separation unit in the MBR. The membrane had effective area of 1.0 m^2 and an average pore size of 0.1 μm. Membrane flux of 30 L m^{-2} h^{-1} was maintained with two calibrations conducted each day. The sludge retention time (SRT) and hydraulic retention time (HRT) for the MBR were 45 d and 5.5 h, respectively. The virgin PVDF membrane and sludge foulants in the MBR were sampled for study.

2.2. Analytical methods

Following procedure was used to prepare the membrane samples: 2 cm × 4 cm membrane pieces were first cut from a large piece of virgin membrane, and then pressed tightly to flatten the surface within two glass slides and mounted with the glass slides. Thereafter, the mounted membranes were transferred to a desiccator for 24 h in order to get rid of the excess water. The sludge samples were pretreated before the measurements with the following process: a stirred cell (Model 8200, Amicon) was used for filtration of sludge suspension obtained from the MBR to form sludge lawns. The resulted sludge lawns were fixed within two glass slides to form relatively flat surface, and then dried in a desiccator for 24 h. The prepared samples subjected to the following measurements.

Static contact angles of three probe liquids (ultra-pure water, glycerol and diiodomethane) on the surfaces of the prepared samples were measured using a contact angle meter (Kino industry Co., Ltd., USA) according to the sessile drop method. Surface zeta potential of the sample of sludge foulants was determined using a Zetasizer Nano ZS (Malvern Instruments Ltd., UK). Surface zeta potential of the membrane sample was measured by a Zeta 90 Plus Zeta Potential Analyzer (Brookhaven Instruments, UK). Membrane surface morphology was characterized by an atomic force microscopy (AFM) (NT-MDT). Triplicate measurements were conducted for each measurement item of a sample. Various membrane surface topographies were graphically constructed by MATLAB 2013.

2.3. XDLVO approach

Interfacial interactions between membrane surface and sludge foulants in aqueous medium can be generally described by XDLVO theory [7,30,31], where the total interaction energy includes three individual LW, AB and EL interaction energy. The individual interaction energy per unit area between two differential planar elements of the surfaces ($\Delta G^{LW}(h)$, $\Delta G^{AB}(h)$ and $\Delta G^{EL}(h)$) is given by:

$$\Delta G^{LW}(h) = -\frac{A_H}{12\pi h^2} = \Delta G_{h_0}^{LW}\frac{h_0^2}{h^2} \tag{1}$$

$$\Delta G^{AB}(h) = \Delta G_{h_0}^{AB}\exp\left(\frac{h_0 - h}{\lambda}\right) \tag{2}$$

$$\Delta G^{EL}(h) = \epsilon_r\epsilon_0\kappa\zeta_f\zeta_m\left(\frac{\zeta_f^2 + \zeta_m^2}{2\zeta_f\zeta_m}(1 - \coth\kappa h) + \frac{1}{\sinh\kappa h}\right) \tag{3}$$

where h is the separation distance between two differential surface elements. Two differential planar elements of the surfaces are generally assumed to contact each other at a hypothetical minimum equilibrium cut-off distance (h_0) [32]. The individual interaction energy per unit area at h_0 ($\Delta G_{h_0}^{LW}$, $\Delta G_{h_0}^{AB}$ and $\Delta G_{h_0}^{EL}$) is obtained by:

$$\Delta G_{h_0}^{LW} = -2\left(\sqrt{\gamma_m^{LW}} - \sqrt{\gamma_w^{LW}}\right)\left(\sqrt{\gamma_f^{LW}} - \sqrt{\gamma_w^{LW}}\right) \tag{4}$$