



Tuning anti-adhesion ability of membrane for a membrane bioreactor by thermodynamic analysis



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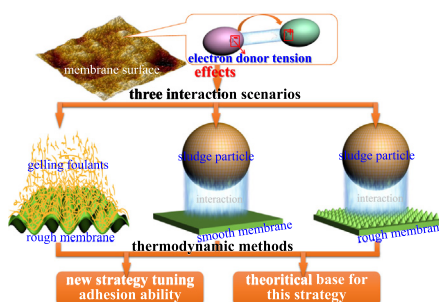
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HIGHLIGHTS

- Electron donor tension is a reliable indicator predicting adsorptive fouling.
- There exists a critical electron donor tension above that interaction is repulsive.
- Membrane surface zeta potential exerts certain effects on adsorptive fouling.
- A new strategy to tune membrane anti-adhesion ability is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Developing strategies that allow tuning anti-adhesion ability of membranes in membrane bioreactors (MBRs) is of primary interest in membrane fouling research. In this study, interaction energies between foulants and membrane in three different interaction scenarios were systematically assessed based on thermodynamic methods. It was found that, membrane surface electron donor tension (γ^-) rather than surface hydrophilicity was a more reliable indicator to predict adsorptive fouling. The interaction energy would be continuously repulsive in the initial range of separation distance when membrane γ^- is higher than a critical value, suggesting that designing membrane with γ^- higher than a critical value would confer membrane with high anti-adhesion ability. It was also found that, zeta potential on the membrane surface exerted certain effects on adsorptive fouling. This study proposed a novel strategy regarding adjusting membrane γ^- to tune anti-adhesion ability of membrane, and also offered a thermodynamic theoretical background to this strategy.

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1. Introduction

Membrane bioreactor (MBR) technology is increasingly used for wastewater treatment and recycling due to its various distinct merits such as high quality effluent, low footprint and low sludge yield (Lin et al., 2012; Wang et al., 2014). However, sustainable manipulation of MBRs always encounters the problem of

membrane fouling (Wang et al., 2008; Lin et al., 2014). Mitigating membrane fouling has been a long primary interest for MBR systems (Wang et al., 2008; Lin et al., 2014). Membrane fouling in MBRs is initiated by adhesion of foulants to membrane surface, followed by the formation of a confluent foulant layer on membrane surface (Meng et al., 2009; Chen et al., 2012a; Wang et al., 2014). Understanding and control of foulant adhesion process appears the key to membrane fouling mitigation. A sound strategy to alleviate membrane fouling is to confer the membrane surface with anti-adhesion ability.

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Nomenclature

D	closest distance between a particle and a planar surface (nm)	λ	decay length of AB interactions in water (0.6 nm)
$f(r, \theta)$	local amplitude directly below the circular arc as a function of the position of the differential circular arc defined by r and θ	ϕ	contact angle ($^\circ$)
h	separation distance between two planar surfaces (nm)	θ	angle of the circular arc in the circular ring
e	electron charge (1.6×10^{-19} C)	ξ	zeta potential (mV)
k	Boltzmann's constant (1.38×10^{-23} J K $^{-1}$)	<i>Superscripts</i>	
ΔG	interaction energy per unit area (mJ m $^{-2}$)	AB	Lewis acid-base
R	radius of foulant particle (μ m)	EL	electrostatic double layer
r	radius of differential circular ring on particle surface (μ m)	LW	Lifshitz-van der Waals
s	roughness of membrane surface (nm)	tol	total
U	interaction energy between membrane surface and particle (kT)	+	electron acceptor
<i>Greek letters</i>		–	electron donor
$\epsilon_r \epsilon_0$	permittivity of the suspending liquid (C V $^{-1}$ m $^{-1}$)	<i>Subscripts</i>	
γ	surface tension parameter (mJ m $^{-2}$)	f	foulant particle
κ	reciprocal Debye screening length (nm $^{-1}$)	h_0	minimum equilibrium cut-off distance (0.158 nm)
		l	liquid
		m	membrane
		s	solid
		w	water

It is generally accepted that interfacial interactions between foulants and membrane surface, which can be depicted by XDLVO approach (van Oss, 1995; Brant and Childress, 2002; Hong et al., 2013), are critical predictors for the susceptibility of a membrane to foulants adhesion (Whang et al., 2012; Hong et al., 2013). For a given MBR, the interfacial interactions are directly determined by the membrane surface properties. In this context, it is possible to control interfacial interactions and adsorptive fouling by properly designing membrane surface properties. The interfacial interactions depend on the surface properties of both foulants and membrane. The foulants prevailed in MBRs fall into two categories: gelling foulants (mainly consist of colloids and solutes) and sludge foulants (Meng et al., 2009; Lin et al., 2012). The different types of foulants have different chemical and morphological properties (Meng et al., 2009; Lin et al., 2012). Meanwhile, the surfaces of membranes commonly used in MBRs are generally rough (Chen et al., 2012b; Zhao et al., 2016). The diversity of foulants and membranes yields different interaction scenarios in MBRs. However, XDLVO approach is only applicable to the scenario of interaction between two infinite planar surfaces (van Oss, 1995).

Moreover, a common strategy reported in literature is to improve membrane surface hydrophilicity (Kang and Cao, 2014). This strategy works well on many occasions. It was reported that, by using series plasma treatments, the surface hydrophilicity and antifouling ability of the modified membranes were simultaneously improved (Yu et al., 2005). Meanwhile, it was also frequently reported the failure of this strategy to actually improve the anti-adhesion ability of membranes (Choo and Lee, 1996; Chen et al., 2012b; Subhi et al., 2012; Zhang et al., 2015). For example, Chen et al. (2012b) reported that the most hydrophilic cellulose acetate (CA) membrane corresponded to largest flux decrease rate as compared with the hydrophobic membranes. Zhang et al. (2015) reported that there is no definite relationship between the membrane surface hydrophilicity and the total interaction energy between particle foulants and membrane. The conflicting results suggest that the strategy of improving membrane hydrophilicity may be not suitable to all the interaction scenarios. This situation, together with the limitation of XDLVO approach, highly demonstrates the necessary to develop series methods for quantitatively assessing interfacial interactions in various scenarios, and also to propose more effective fouling control strategies.

Through rigorous modeling of membrane surface morphology, combining with surface element integration (SEI) method and the composite Simpson's approach, a novel method, which allows quantitative calculation of interfacial interactions between rough membrane surface and foulant particles, has been recently developed (Zhao et al., 2016). This method may provide a toehold in tuning anti-adhesion ability of membranes. However, to date, no specific study has been conducted on this topic. Therefore, it is quite desirable and attractive to perform a conceptual design of anti-adhesion membranes based on thermodynamic methods, although it is currently still an enormous challenge.

In this study, the membrane and foulants typical for MBR systems were characterized, and the interfacial interactions between membrane and foulants were assessed. Effects of membrane surface properties on the interfacial interactions were analyzed. The results were then used to design membranes with high anti-adhesion ability in MBRs. This study offered a strong guidance for fabrication and selection of membranes used in MBRs.

2. Materials and methods

2.1. Experimental setup and operation

A lab-scale submerged MBR (SMBR) setup with 65 L effective volume (dimensions of 0.54 m height \times 0.30 m length \times 0.40 m width) was continuously operated for more than 400 days. Synthetic municipal wastewater was used as influent with the following composition: 300 mg COD/L glucose plus the following mineral medium: Na₂CO₃ (46 mg Na/L); NaHCO₃ (23 mg Na/L); (NH₄)₂SO₄ (27 mg N/L); KH₂PO₄ (7 mg P/L); MgSO₄ (7 mg Mg/L); CaCl₂ (6 mg Ca/L); FeCl₃ (4 mg Fe/L); ZnCl₂ (0.11 mg Zn/L); CoCl₂ (0.1 mg Co/L); NaMoO₄ (0.07 mg Mo/L); MnSO₄ (0.04 mg Mn/L) and CuSO₄ (0.03 mg Cu/L). 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 μ m. An air diffuser was located underneath the membrane module to provide aeration with specific aeration demand per permeate product (SAD_p) of about 180 m³_{air}/m³_{permeate}. A peristaltic pump operated in an intermittent mode (4 min-on

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