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Thermodynamic analysis of effects of contact angle on interfacial interactions and its implications for membrane fouling control

Jianrong Chen [a], Liguo Shen [a], Meijia Zhang [a], Huachang Hong [a], Yiming He [b], Bao-Qiang Liao [c], Hongjun Lin [a,*]

[a] College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua 321004, PR China
[b] Department of Materials Physics, Zhejiang Normal University, Jinhua 321004, PR China
[c] Department of Chemical Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada

HIGHLIGHTS

- Total interaction energy monotonically decreases with water contact angle.
- Total interaction energy monotonically increases with glycerol contact angle.
- Water and glycerol contact angle are reliable indicators predicting interaction.
- Membrane roughness remarkably decreases interaction strength.
- Diiodomethane contact angle has minor effect on the total interaction.

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ABSTRACT

Concept of hydrophobicity always fails to accurately assess the interfacial interaction and membrane fouling, which calls for reliable parameters for this purpose. In this study, effects of contact angle on interfacial interactions related to membrane fouling were investigated based on thermodynamic analysis. It was found that, total interaction energy between sludge foulants and membrane monotonically decreases and increases with water and glycerol contact angle, respectively, indicating that these two parameters can be reliable indicators predicting total interaction energy and membrane fouling. Membrane roughness decreases interaction strength for over 20 times, and effects of membrane roughness on membrane fouling should consider water and glycerol contact angle on membrane. It was revealed existence of a critical water and glycerol contact angle for a given membrane bioreactor. Meanwhile, diiodomethane contact angle has minor effect on the total interaction, and cannot be regarded as an effective indicator assessing interfacial interactions and membrane fouling.

1. Introduction

Membrane bioreactor (MBR) is an efficient technology for wastewater treatment and reuse. Unfortunately, membrane fouling, which can lead to membrane flux decline and cost increase, remains a serious hamper for widespread application of this technology (Lin et al., 2014b; Meng et al., 2009; Wang et al., 2014). Membrane fouling mechanisms and its control strategies have been long-lasting research issues since MBR technology was invented.

It is widely accepted that interfacial interactions between foulants and membrane surface are critical predictors for the susceptibility of a membrane to foulants adhesion (Hong et al., 2013; Wang et al., 2013; Whang et al., 2012), which is highly related to membrane fouling. Interfacial interactions between two substances in a media can be generally depicted by XDLVO theory (van Oss, 1995, 1997), where Lifshitz–van der Waals (LW), acid–based (AB), and electrostatic double layer (EL) interactions are included. Membrane surface properties play important roles as they determine the magnitude and sign (attractive/repulsive) of the interfacial interactions between membrane surface and foulants. Hydrophobicity as well as surface roughness and charge (zeta potential) is primary membrane surface properties. In XDLVO theory, hydrophobicity of a material is quantitatively defined as the free energy of interaction between two identical surfaces immersed in water (ΔG_{sws}) (van Oss, 1995). A frequent operation to qualify membrane hydrophobicity is contact angle measurements with probe liquids (Feng et al., 2009; van Oss, 1997; Wang et al., 2013).

* Corresponding author. Tel.: +86 0579 82282273.
E-mail address: hjlin@zjnu.cn (H. Lin).

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Nomenclature

D	closest distance between a particle and a planar surface (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
h	separation distance between two planar surfaces (nm)
e	electron charge (1.6×10^{-19} C)
k	Boltzmann's constant (1.38×10^{-23} J K^{-1})
ΔG	interaction energy per unit area (mJ m^{-2})
R	radius of foulant particle (μm)
r	radius of differential circular ring on particle surface (μm)
s	roughness of membrane surface (nm)
U	interaction energy between membrane surface and particle (kT)
Greek letters	
$\varepsilon_r\varepsilon_0$	permittivity of the suspending liquid (C V^{-1} m^{-1})
γ	surface tension parameter (mJ m^{-2})
κ	reciprocal Debye screening length (nm^{-1})
λ	decay length of AB interactions in water (0.6 nm)
ϕ	contact angle (°)
θ	angle of the circular arc in the circular ring
ζ	zeta potential (mV)
Superscripts	
AB	Lewis acid–base
EL	electrostatic double layer
LW	Lifshitz–van der Waals
tol	total
+	electron acceptor
−	electron donor
Subscripts	
f	foulant particle
h_0	minimum equilibrium cut-off distance (0.158 nm)
l	liquid
m	membrane
s	solid
w	water

In contrast to many studies devoted to study the effects of hydrophobicity on membrane fouling, to our knowledge, no specific study has been conducted to study the effects of contact angle on membrane fouling although contact angle is an index of hydrophobicity. Moreover, hydrophobicity defined by ΔG_{sws} has been frequently reported to fail to accurately predict membrane performance (Chen et al., 2012; Subhi et al., 2012). For example, it was observed that hydrophilic foulants were closely associated with irreversible fouling of low-pressure membrane, while hydrophobic foulants strongly adsorbed on the hydrophobic membrane surface (Yamamura et al., 2007). Chen et al. (2012) reported that the most hydrophilic cellulose acetate (CA) membrane corresponded to largest flux decrease rate as compared with polyvinylidene fluoride (PVDF) and polyethersulfone (PES) membranes. These phenomena maybe not surprising as considering the information loss when contact angle is used to qualify hydrophobicity, and the fact that hydrophobicity is not an independent membrane surface property affecting interfacial interactions. Nonetheless, these studies demonstrated the limitation of the hydrophobicity concept in explaining fouling phenomena and the demand for suitable parameters/methodologies enable to assess interfacial interactions.

In practice, in order to quantitatively characterize membrane hydrophobicity, contact angle measurements are generally performed with three common probe liquids including one apolar (diiodomethane (CH_2I_2)) and two polar probe liquids (water and glycerol) according to XDLVO theory (Brant and Childress, 2002; van Oss, 1995). The contact angle data possess more abundant information than hydrophobicity itself. Moreover, it was reported that other membrane surface properties including surface roughness and charge also played important roles in interfacial interactions. Therefore, it is anticipated that investigating the effects of contact angle under conditions of different other surface properties would provide a more justified and comprehensive insight into the complex interactions between membrane and foulants.

In the current study, the surface properties of PVDF membranes and sludge foulants obtained from a MBR treating synthetic municipal wastewater were experimentally determined. Effects of contact angles of three probe liquids on membrane surface on interfacial interactions under different interaction scenarios were systematically assessed by series methods. The implications of the obtained results for membrane fouling mitigation were also discussed.

2. Methods

2.1. Experimental setup and operation

A lab-scale submerged MBR (SMBR) with an effective volume of 65 L ($0.54 \times 0.30 \times 0.40$) was continuously operated to provide the sludge samples needed. A flat sheet membrane model with five membrane elements was vertically located in the bioreactor. The total effective filtration area was 0.1 m^2. The membrane applied was made from PVDF material, which was considered as a material with longer durability and lower fouling tendency than other materials (Lin et al., 2009). In order to maintain the growth of microorganism and mitigate the membrane fouling, an aeration was placed under the membrane module to provide adequate oxygen and membrane surface scouring stress. The permeate liquid was collected by a peristaltic pump operated in an intermittent suction mode of 4-min-on and 1-min-off. The membrane flux was controlled at 30 L/(m^2 h) with twice calibrations every day, corresponding to a hydraulic retention time (HRT) of 5.5 h.

2.2. Analytic methods

A contact angle meter (Kino industry Co., Ltd., USA) was used to measure the static contact angles of three probe liquids including ultrapure water, glycerol and diiodomethane on membrane and sludge foulant samples. The measurements were according to the sessile drop method. The membrane samples were prepared as follows: a large piece of virgin membrane was cut into small membrane pieces with dimension of 2 cm × 4 cm. The resulted membrane pieces were pressed tightly to flatten the surface within two glass slides, and were then mounted with the glass slides. This membrane was viewed as smooth membrane. After fastened with drawstrings, the mounted membranes were placed into a desiccator to get rid of excess water for 24 h. The sludge samples were pretreated before the measurements with the following process: sludge suspension obtained from the MBR was filtrated by a stirred