Natural organic matter fouling behaviors on superwetting nanofiltration membranes

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ABSTRACT

Nanofiltration has been widely recognized as a promising technology for the removal of micro-molecular organic components from natural water. Natural organic matter (NOM), a very important precursor of disinfection by-products, is currently considered as the major cause of membrane fouling. It is necessary to develop a membrane with both high NOM rejection and anti-NOM fouling properties. In this study, both superhydrophilic and superhydrophobic nanofiltration membranes for NOM removal have been fabricated. The fouling behavior of NOM on superwetting nanofiltration membranes has been extensively investigated by using humic acid (HA) as the model foulant. The extended Derjaguin−Landau−Verwey−Overbeek approach and nanoindentor scratch tests suggested that the superhydrophilic membrane had the strongest repulsion force to HA due to the highest positive total interaction energy (ΔG^{TOT}) value and the lowest critical load. Excitation emission matrix analyses of natural water also indicated that the superhydrophilic membrane showed resistance to fouling by hydrophobic substances and therefore high removal thereof. Conversely, the superhydrophobic membrane showed resistance to fouling by hydrophilic substances and therefore high removal capacity. Long-term operation suggested that the superhydrophilic membrane had high stability due to its anti-NOM fouling capacity. Based on the different anti-fouling properties of the studied superwetting membranes, a combination of superhydrophilic and superhydrophobic membranes was examined to further improve the removal of both hydrophobic and hydrophilic pollutants. With a combination of superhydrophilic and superhydrophobic membranes, the NOM rejection (R_{UV254}) and DOC removal rates (R_{DOC}) could be increased to 83.6% and 73.3%, respectively.

1. Introduction

In natural water, natural organic matter (NOM) can affect the color, taste and odor of raw water, moreover, it has been identified as precursors of disinfection by-products. NOM can be divided into three categories: humic acid (HA), fulvic acid (FA) and humin, with molecular weights ranging from <1 kDa to >500 kDa (Jaouadi et al., 2012; Lee et al., 2004; Ng et al., 2013). Nanofiltration has been widely recognized as a promising technology to remove NOM from natural water due to its high efficiency for removal of pollutants, low energy consumption, and easy accessibility. With the improvement of drinking water standards and the industrialized application of membrane technology, it is critical to develop novel nanofiltration membranes with high NOM removal and stability. Concurrently, the biggest challenge is the inevitable occurrence of membrane fouling, which is caused by the NOM accumulation on the membrane surface during the NOM removal process in drinking water treatment and production (Al-Amoudi, 2010; Cai et al., 2008; Cai and Benjamin, 2011; Howe and Clark, 2002; Huang et al., 2012; Jermann et al., 2007, 2008; Lahoussine-Turcaud et al., 1990; Saravia et al., 2006; Van der Bruggen et al., 2003; Vrouwenvelder et al., 1998; Yang et al., 2010; Zhang et al., 2003b; Zhou et al., 2009). In particular, HA has been considered as the most important foulant for the membrane flux decline.

Membrane fouling is an issue of interface action between the foulant, membrane, and solution. NOM fouling is mainly determined by the interface relationship between NOM and the

membrane surface in aqueous solution. Many studies have been carried out to investigate this point; however, the effect of hydrophilicity/-phobicity of NOM and the membrane surface on fouling behavior is still a controversial issue. Some researchers have studied the effect of NOM hydrophilicity/-phobicity on membrane fouling, since NOM can be fractionated into relatively hydrophilic and hydrophobic components (Hao et al., 2011; Kilduff et al., 2004; Mänttäri et al., 2000; Thorsen, 2004). Amy and Nilson found that the hydrophobic fraction was the major factor for flux decline, while the hydrophilic fraction was much less responsible for fouling of the membrane (Amy and Cho, 1999; Nilson and DiGiano, 1996). In contrast, Cho et al. (2000), Fan et al. (2001) and Yamamura et al. (2014) obtained completely opposite results, and they found that the hydrophilic fractions induced more severe loss of membrane permeability than the hydrophobic fractions. Although some previous studies indicated that hydrophilicity/-phobicity of the membrane surface was a predominant influence on the extent of fouling in aqueous systems (Maximous et al., 2009; Xiao et al., 2011), contradictory results were also often be obtained. Zhang et al. (2003a) reported that with the increase of surface hydrophobicity, a smaller amount of HA was deposited onto the membrane surface and the permeate flux reduction decreased. Conversely, many reports have indicated that a hydrophilic surface favors less fouling, due to a strong hydration layer that repels the adsorption of foulants on the membrane surface (Mänttäri et al., 2000; Tiraferri et al., 2012). Thus, determining the effect of hydrophilicity/-phobicity of NOM and membrane surface wettability on its fouling behavior is still a challenge.

To date, most studies in this field have concerned in the wettability of membranes with water contact angles in the range $30-120°$, covering the range from hydrophilic to hydrophobic surfaces. It is notable that some extraordinary membrane performances have been achieved when the wettability was extended to superhydrophilicity or superhydrophobicity. It is generally accepted that the solid surfaces with contact angles $<5°$ can be treated to be superhydrophilic while those $>150°$ are defined as superhydrophobic. Tiraferri et al. (2012) and Liang et al. (2014) investigated the fouling behavior of superhydrophilic membranes with model wastewater and found that these membranes showed lower overall flux decline and anti-fouling properties. Our previous study indicated that the pervaporation flux of a superhydrophilic membrane was twice than that of a hydrophilic membrane (Gong et al., 2014). We also demonstrated that the superhydrophobic pervaporation membrane showed both higher selectivity and higher permeability than a hydrophobic membrane (Li et al., 2014). However, little work has dealt with superwetting nanofiltration membranes for NOM removal from natural water. Additionally, there has been no systematic work on NOM fouling behavior on superwetting nanofiltration membranes.

The aim of this study is to develop the superwetting nanofiltration membranes with both high NOM rejection and good anti-NOM fouling properties. We extensively studied the NOM fouling behavior on superwetting nanofiltration membranes. The interaction forces and free energy of HA adhesion on superwetting membrane surfaces were elucidated by the extended Derjaguin−Landau−Verwey−Overbeek (XDLVO) thermodynamic analyses. Then we carried out the nanoindentor scratch tests to quantify the adhesion between the HA fouling layer and membrane surface. In addition, the NOM fouling of hydrophilic and hydrophobic components on superhydrophilic and superhydrophobic nanofiltration membranes were analyzed by excitation emission matrix (EEM). The natural water treatment performances of the superwetting membranes and their long-term stability were investigated using real reservoir water.

2. Theoretical

The XDLVO model has widely been used to explain how aqueous foulants interact with surfaces of polymeric membranes (Brant and Childress, 2002; Kang et al., 2004; Kim et al., 2006). According to XDLVO theory, in an aquatic environmental system, the interfacial energy between a membrane and foulants is the sum of the Lifshitz−van der Waals, Lewis acid−base, and electrostatic double-layer interactions, which is given by (Brant and Childress, 2002):

$$G_{mwf}^{TOT} = G_{mwf}^{LW} + G_{mwf}^{AB} + G_{mwf}^{EL} \tag{1}$$

where G_{mwf}^{TOT} is the total interaction energy between the membrane and foulants and G_{mwf}^{LW}, G_{mwf}^{AB} and G_{mwf}^{EL} represent the Lifshitz−van der Waals, Lewis acid−base, and electrostatic double-layer free energies, respectively. The subscripts m, w, and f correspond to the membrane, water, and the foulant, respectively.

2.1. Surface tension components

The surface tension components of the membrane and foulants are determined from the extended Young equation (Bouchard et al., 1997; Gourley et al., 1994; Van Oss and Good, 1988), which gives their relationship with the contact angle of a liquid on a solid surface. The surface tension parameters of both the solid and liquid can be written as follows:

$$(1 + \cos\theta)\gamma^{TOT} = 2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_l^+\gamma_s^-}\right) \tag{2}$$

$$\gamma^{AB} = 2\sqrt{\gamma^+}\sqrt{\gamma^-} \tag{3}$$

$$\gamma^{TOT} = \gamma^{LW} + \gamma^{AB} \tag{4}$$

where θ is the contact angle, γ^{TOT} is the total surface tension, γ^{LW} is the Lifshitz−van der Waals component, and γ^+ and γ^- are the electron-acceptor and electron-donor components, respectively. The subscripts s and l correspond to the solid surface and liquid, respectively. The surface tension parameters of foulants (γ_f^+, γ_f^-, γ_f^{LW}) and membranes (γ_m^+, γ_m^-, γ_m^{LW}) can be determined from equation (2) after measuring the contact angle data for three probe liquids with known surface tension parameters (γ_l^+, γ_l^-, γ_l^{LW}).

2.2. Adhesion free energy

The free energy of adhesion per unit area was calculated as follows:

$$\triangle G_{mwf}^{LW} = 2\left(\sqrt{\gamma_w^{LW}} - \sqrt{\gamma_m^{LW}}\right)\left(\sqrt{\gamma_f^{LW}} - \sqrt{\gamma_w^{LW}}\right) \tag{5}$$

$$\triangle G_{mwf}^{AB} = 2\sqrt{\gamma_w^+}(\sqrt{\gamma_m^-} + \sqrt{\gamma_f^-} - \sqrt{\gamma_w^-}) + 2\sqrt{\gamma_w^-}\left(\sqrt{\gamma_m^+} + \sqrt{\gamma_f^+} - \sqrt{\gamma_w^+}\right) - 2\left(\sqrt{\gamma_m^+\gamma_f^-} + \sqrt{\gamma_m^-\gamma_f^+}\right) \tag{6}$$

$$\triangle G_{mwf}^{EL} = \frac{\varepsilon_0\varepsilon_r\kappa}{2}\left(\xi_m^2 + \xi_f^2\right)\left[1 - \coth(\kappa h_o) + \frac{2\xi_m\xi_f}{\xi_m^2 + \xi_f^2}\operatorname{csch}(\kappa h_o)\right] \tag{7}$$

where $\triangle G_{mwf}^{LW}$, $\triangle G_{mwf}^{AB}$ and $\triangle G_{mwf}^{EL}$, expressed in mJ·m^{-2}, are the