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Assessing the effect of surface modification of polyamide RO membrane by L-DOPA on the short range physiochemical interactions with biopolymer fouling on the membrane

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ABSTRACT

Theoretical predictions of interaction energies for membrane–biopolymer foulant pairs were used to compare the fouling tendencies of a virgin commercial polyamide reverse osmosis (RO) membrane with a amino acid 3-(3,4-dihydroxyphenyl)-L-alanine (L-DOPA) coated RO membrane. Lifshitz–van der Waals (LW) and Lewis acid–base (AB) surface tension components of the membranes were determined based on contact angle results using the van Oss approach. From these values, the LW and AB components of the free energy of adhesion between membrane and foulants were calculated. Electrostatic (EL) double layer interaction energies between the membrane and foulants were also estimated using the measured surface charge data of the membranes and fouling agents. Bovine serum albumin (BSA) and alginic acid sodium salt (alginate) were used as model biopolymers causing membrane fouling. Based on the calculated adhesion free energies, acid–base interactions were found to have the strongest impact on the adhesion of both BSA and alginate to the either membranes surfaces. It was found that L-DOPA modification has significantly lowered acid–base interaction affinity toward the adhesion of both foulants studied. On the basis of calculated free energies of adhesion, lower fouling tendency of the L-DOPA modified membrane was expected. The accelerated fouling tests indicated a lower flux decline rate for the modified membrane and confirmed the results obtained from theory.

1. Introduction

Fouling of reverse osmosis membranes is one of the barriers against their efficient application to produce fresh water from seawater or other water resources. Among different types of materials which cause membrane fouling, organic matter and biopolymers are of the most problematic, because they can pass through the pre-treatment steps and reach the reverse osmosis (RO) membranes [1,2]. Adsorbed organic matter and biopolymers also provide a suitable environment for bacterial growth. Several researchers described that fouling of the membranes by biopolymers and organic matter is influenced by operating conditions [3], feed solution chemistry [4] as well as physicochemical properties of organic matter and membranes [5].

Prevention of adhesion of foulants has been an effective strategy to control membrane fouling. Therefore, modification of the membrane surface to make it unfavorable for adhesion has been proposed as a strategy to reduce the membrane fouling rate [6–8]. In our past study, surface modification of the RO membrane with L-DOPA was carried out to alter the membrane surface [9]. Modified membranes showed a lower flux decline rate compared to the virgin membrane in an accelerated fouling test using a mixture of BSA and alginate as model biopolymers. Since modification with L-DOPA can be performed in situ, this approach is of particular interest in practical applications. The goal of this investigation is to obtain a more in depth insight into the effect of L-DOPA modification on the interfacial interactions leading to the inception of fouling.

In this study, the thermodynamic work of adhesion which quantifies the energy available for adhesion is calculated using the concept developed by Fowkes [10] and later by van Oss [11]. The calculated energy of adhesion is then related to the propensity of

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Abbreviations: AB, Lewis acid–base; BSA, bovine serum albumin; EL, electrostatic double layer; f, foulant; IEP, isoelectric point; L-DOPA, 3-(3,4-dihydroxyphenyl)-L-alanine; LW, Lifshitz–van der Waals; PA, polyamide; RO, reverse osmosis; s, solid; w, water; XDLVO, extended Derjaguin–Landau–Verwey–Overbeek.

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Greek symbols

ΔG_{AB}	Lewis acid–base free energy of interaction
ΔG_{EL}	electrostatic double layer free energy of interaction
ΔG_{LW}	Lifshitz–van der Waals free energy of interaction
ΔG_{TOT}	total free energy of interaction
ΔG_{sws}	cohesive free energy
γ^{+}	electron-acceptor component of the surface free energy
γ^{-}	electron-donor component of the surface free energy
γ^{AB}	Lewis acid–base component of the surface free energy
γ^{LW}	Lifshitz–van der Waals component of the surface free enrgy
$\in_0$	vacuum permittivity
$\in_r$	relative permittivity of water
κ	inverse Deby screening length
γ	surface free energy
ψ	surface potential

the adhered biopolymers. This theory has been frequently used to describe colloidal attachment to the membrane surface [12,13]. Lee et al. [14] used this theory to study fouling of ultrafiltration membranes by natural organic matter (NOM). They also used this method to elucidate the mechanism of organic matter fouling on a commercial RO membrane [15]. Application of this approach for NOM is based on the hypothesis that dissolved natural organic matter behave like colloidal particles. Botton et al. [16] used this theory to predict the pharmaceuticals rejection by virgin and biofouled nanofiltration membranes. They found that pharmaceuticals rejection directly correlates with the free energy of interaction between membranes studied and pharmaceuticals dissolved in the water phase.

The objectives of the present research are therefore two-fold: (i) to characterize the effect of L-DOPA modification on the surface properties of the membrane and consequently on the interactions between membrane and biopolymers, and (ii) to investigate how the alterations in interaction parameters affect membrane fouling behavior.

2. Theory

2.1. Interaction energies

The Extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory suggested by van Oss was applied to calculate the total energy needed to bring organic matter from an infinite distance to a membrane surface immersed in water. According to the XDLVO theory, the interfacial energies in an aqueous system can be described as the sum of:

(i) Apolar or Lifshitz–van der Waals (LW) energies
(ii) Polar or Lewis acid–base (AB) energies
(iii) Electrostatic double layer (EL) energies
(iv) Brownian movement (BR) energies.

The contribution of Brownian motion energy, resulting from thermal energy of molecules, is very small compared to the other interaction energies. Therefore, the total free energy of interaction is written as:

$$\Delta G_{\text{TOT}} = \Delta G_{\text{LW}} + \Delta G_{\text{AB}} + \Delta G_{\text{EL}} \tag{1}$$

where ΔG_{LW} represents the Lifshitz–van der Waals energy, ΔG_{AB} is the acid–base interaction energy and ΔG_{EL} refers to the electrostatic energy. From a thermodynamic point of view, adhesion or attraction occurs when ΔG_{TOT} is negative, whereas repulsion occurs when ΔG_{TOT} is positive.

Application of this approach to estimate the free energy of adhesion requires the determination of surface tension components and measurement of surface charges of the membranes and relevant fouling agents.

2.2. Surface tension components

van Oss expressed the total surface tension as the sum of Lifshitz–van der Waals (γ^{LW}) and Lewis acid–base (γ^{AB}) components of the surface tension [11].

$$\gamma^{\text{TOT}} = \gamma^{\text{LW}} + \gamma^{\text{AB}} \tag{2}$$

The AB component of a material surface energy is given by:

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

γ_s^{+} is the electron acceptor parameter and γ_s^{-} is the electron donor parameter.

The Young equation links the contact angle of a drop of liquid (l) deposited on a flat solid surface (s) with the surface tension of the liquid and the solid surface [17]. It is expressed as:

$$\gamma_s = \gamma_{ls} + \gamma_l \cos\theta \tag{4}$$

Dupre expressed the work required to separate these two surfaces from contact as [18]:

$$\Delta G_{ls} = \gamma_{ls} - \gamma_l - \gamma_s \tag{5}$$

The Young–Dupre equation is then obtained from Eqs. (4) and (5):

$$\Delta G_{ls} = -\gamma_l(1 + \cos\theta) \tag{6}$$

The complete Young–Dupre equation in terms of the interfacial tension components is obtained as discussed by van Oss [11]:

$$\gamma_l(1 + \cos\theta) = \left(\sqrt{\gamma_s^{\text{LW}}\gamma_l^{\text{LW}}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}}\right) \tag{7}$$

Consequently, the unknown surface tension components of a solid surface can be determined by performing contact angle measurements using three probe liquids with known surface tension component parameters.

2.3. Determination of free energy of adhesion

Using the Young–Dupre equation, the surface tension components of the membranes (m) and model foulants (f) can be determined. These surface tension parameters are then used to calculate the free energy of adhesion between membrane and foulants immersed into water. The LW and AB components of free energy per unit area can be expressed as [11]:

$$\Delta G_{\text{mwf}}^{\text{LW}} = 2\left(\sqrt{\gamma_w^{\text{LW}}} - \sqrt{\gamma_m^{\text{LW}}}\right)\left(\sqrt{\gamma_f^{\text{LW}}} - \sqrt{\gamma_w^{\text{LW}}}\right) \tag{8}$$

$$\begin{aligned}\Delta G_{\text{mwf}}^{\text{AB}} = {} & 2\sqrt{\gamma_w^{+}}\left(\sqrt{\gamma_m^{-}} + \sqrt{\gamma_f} + \sqrt{\gamma_w^{-}}\right)\\ & +2\sqrt{\gamma_w^{-}}\left(\sqrt{\gamma_m^{-}} + \sqrt{\gamma_f^{+}} + \sqrt{\gamma_w^{-}}\right)\\ & -2\sqrt{\gamma_m^{+}\gamma_f^{-}} - 2\sqrt{\gamma_f^{+}\gamma_m^{-}}\end{aligned} \tag{9}$$

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