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Influence of solution chemistry on the surface heterogeneity of reverse osmosis membrane

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ABSTRACT

The chemical heterogeneity of reverse osmosis membrane surface and its impacts on membrane fouling were investigated using dynamic hysteresis, which is a newly developed surface analytical technique. Based on dynamic hysteresis measurements, it has been demonstrated that the chemical heterogeneity of membrane surface was greatly influenced by solution—pH and ionic strength. Significant variation of dynamic hysteresis was observed as solution pH changed, implying the alteration of membrane surface heterogeneity. Interestingly, there existed the interplay between chemical and physical surface heterogeneity with respect to solution ionic strength. At low ionic strength, dynamic hysteresis mostly reflected chemical surface heterogeneity, while physical surface heterogeneity played more dominant role in the change of dynamic hysteresis with increasing ionic strength. This implies that membrane fouling due to chemical surface heterogeneity of the membrane is less remarkable in seawater desalination compared to wastewater and brackish water treatments. In addition, mechanisms and factors affecting chemical and physical surface heterogeneity and their interplay with respect to solution chemistry including pH, ionic strength and divalent cation concentration are discussed and elucidated.

Keywords: Membrane surface characterization; Dynamic hysteresis; RO membrane; Chemical heterogeneity

1. Introduction

Reverse osmosis (RO) process has been considered as one of the most promising technologies and developed significantly over the past few decades. Efficient operation of RO process, however, is often hampered by membrane fouling. There are several factors affecting membrane fouling such as membrane surface characteristics, feed water solution chemistry and foulant properties. In the aspect of membrane surface characteristics, both chemical (i.e. surface charge and hydrophobicity) and physical (i.e. surface roughness) factors are closely related to the rate and extent of membrane fouling [1–3]. Regarding to the solution chemistry, ionic strength, pH and divalent cations have been reported to be the key factors affecting natural organic matter fouling [4]. Interestingly, the impact of solution chemistry on membrane fouling was less influential in seawater desalination compared to drinking and wastewater treatments [5]. In terms of foulant properties, foulants with higher adhesive

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interaction force with membrane showed greater fouling potential [6]. Among these various factors affecting membrane fouling, membrane surface characteristics are relatively easy to be enhanced during membrane synthesis and, thus, the effort to characterize and modify membrane surface is of practical importance for reducing membrane fouling.

Membrane surface charge is determined usually by measuring zeta potential which has been widely used to predict the fouling potential of RO membranes [7–10]. However, using the Helmholtz–Smoluchowski equation or the Fairbrother–Mastin equation for relating zeta potential to measured streaming potential has a limitation to determine zeta potential at high ionic strength due to the theoretical limit for electro-kinetic phenomena [11–13]. Further, the prediction of membrane fouling based on zeta potential often fails, since zeta potential only provides an averaged surface charge without reflecting the charge distribution on the membrane surface [14,15].

Previous studies investigating particle transport and deposition showed that theoretical deposition distribution rates calculated with electric double layer theories cannot be utilized directly to predict particle mobility in aquatic environments, since particles tend to preferentially deposit onto the specific locations of collector surfaces [3,16–18]. Song et al. described surface charge heterogeneity using patchwise and random distribution models and suggested that surfaces with charge heterogeneity exhibit larger particle deposition rates than those with no charge heterogeneity [16]. They also suggested that the change in particle deposition rate with time is strongly influenced by the heterogeneity of porous media surfaces [17].

Until recently, a limited number of studies investigating the surface chemical heterogeneity of the membrane have been performed in spite of its importance. Sakuma et al. introduced the charge distribution of poly (N,N-L-lysinediylterephthaloyl) microcapsule membranes using zeta potential measurements at various pH and ionic strengths of the medium [15]. Brant et al. identified and mapped the functionality of membrane surfaces using Atomic force microscopy (AFM), and suggested that membrane surface chemical heterogeneities are important in colloid transport [14].

Recently, dynamic hysteresis was introduced as a measure of analysing membrane surface heterogeneity. Lee et al. demonstrated that dynamic hysteresis could be a useful parameter to characterize the physical surface heterogeneity of RO membranes [19]. In addition, it was shown that dynamic hysteresis could be adopted as a valuable tool to analyse the chemical heterogeneity of the membrane surface and is directly related to increase in both membrane fouling potential and dynamic hysteresis [20]. It was also shown that dynamic hysteresis measurements could be performed under various solution chemistry conditions, and a more accurate correlation between dynamic hysteresis and physical and chemical surface heterogeneity could be obtained by using a non-polar and polar liquid, respectively. However, the relationship between dynamic hysteresis and membrane surface heterogeneity has not been explored further under various solution chemistries such as high ionic strength similar to seawater total dissolved solids (TDS) condition.

The objective of this study is to investigate the alteration of the membrane surface heterogeneity with respect to the solution pH and ionic strengths ranging from freshwater to seawater by assessing the chemical and physical surface heterogeneity of RO membrane through dynamic hysteresis. In addition, surface characteristics of RO membrane, including zeta potential, contact angle and roughness, were determined and compared to dynamic hysteresis. Lastly, the implication of dynamic hysteresis measurements to membrane fouling is discussed and delineated.

2. Materials and methods

2.1. RO membrane

A commercial RO membrane (ESPA2, Hydranautics) was selected for this research. This membrane is a thin-film composite polyamide membrane which is classified as low-pressure RO typically used for brackish water treatment. RO membrane was immersed and stored in deionized (DI) water at 4°C and DI water was replaced regularly during storage. The membrane was cut into strips measuring 15 mm in width and 20 mm in length for dynamic hysteresis measurements. Prior to each analysis, the membrane was put into 20–25°C DI water for 2 h as all of the analyses in this study were carried out at room temperature. General properties of the membrane in terms of zeta potential, contact angle and surface roughness were determined and listed in Table 1. These results show that ESPA2 membrane has a relatively hydrophobic and smooth surface.

2.2. Solution chemistry

The ionic strength of the test solutions was adjusted with NaCl. NaCl was added to DI water and mixed for 1 h at room temperature (20–25°C). When needed, solution pH was adjusted with 0.1 M of NaOH or HCl stock solutions. Divalent cations (i.e. $CaCl_2$ and $MgCl_2$) were prepared at concentrations of 0.0667 M, which are equivalent to the total ionic

Table 1
General properties of RO membrane used

Membrane	Contact angle (°)	Zeta potential* (mV)	Roughness (nm)
ESPA2	61.3	−26.0	68.61

Note: Measured at pH = 6.5–7.0; Temp. = 20–25°C.

*Zeta potential was determined at the background electrolyte solution of 10 mM KCl.

strength of 0.2 M. All test solutions were freshly prepared 1 h before each experiment.

2.3. Dynamic hysteresis

Dynamic hysteresis was determined based on the Wilhelmy plate method [21]. During the measurement, a membrane sample was held by the automated microbalance, then pushed into or pulled from a test liquid. Therefore, the measured force acting on the membrane sample alternates depending on the direction of movements. The force acting on the membrane sample when pushed into the test liquid is the advancing force and when pulled out from the test liquid is the receding force. The measurements were carried out using a Sigma 701 microbalance (KSV Instrument, Ltd., Finland) interfaced with a PC for automatic control and data acquisition. It was operated by holding a membrane sample attached to microbalance vertically. A liquid cell containing a test liquid moved up and down at constant speed rate repeatedly during the measurements.

All parameters employed during the hysteresis measurements are given by Lee et al. [20]. The surface tension of test liquids was measured at each time by the force du Nouy ring method at the test liquid temperature of 20–22°C and atmosphere temperatures of 20–24°C, with a humidity of 20–25%. The ring was rinsed by ethyl alcohol prior to each measurement.

2.4. Contact angle

Contact angle measurements were performed with a goniometer (DM 500, Kyowa interface Science, Japan). Equilibrium contact angle measurements as described by Marmur [22] were adopted. Equilibrium contact angle was the average of the left and right contact angles. Ten measurements for each membrane were performed. The reported values are the average of 10 equilibrium contact angles.

2.5. Zeta potential

Membrane zeta potential was analysed by a streaming current electrokinetic analyser (SurPass, Anton Paar GmbH, Graz, Austria) following the procedure described by Luxbacher [10]. Zeta potential value was interpreted based on the Fairbrother and Mastin substitution [11]. For the surface zeta potential analysis, 0.01 M KCl was used as a background electrolyte solution and solution pH was varied from 2 to 10. The operating pressure ranged from 0 to 500 mbar and temperature was about 25°C. The zeta potentials listed in Table 1 were the values obtained at pH 7.0.

2.6. Surface roughness

Membrane surface roughness was analysed by AFM imaging (PUCOStation AFM, Surface Imaging Systems, Herzogenrath, Germany). Liquid phase AFM imaging was conducted in contact mode with silicon probes, backside of which had 30 nm thick aluminium reflex coating for better resolution and stability in liquid phase applications (APPNANO, Applied Nano Structures, Inc., Santa Clara, CA). The probe has a spring constant of 0.1 N/m (±0.08 N/m), resonance frequency of 28 kHz (±10 kHz), tip radius of 5–6 nm, tip height of 14 μm (±2 μm), and cantilever length of 225 μm (±10 μm). The RO membranes were immersed in a liquid cell containing pre-adjusted test solution in terms of pH and ionic strength.

The membrane was scanned three times with randomly selecting a scan position. Membranes surface roughness was quantified by root mean square (RMS) roughness, which is the RMS deviation of the peaks and valleys from the mean plane. Approaching force ranged from 4.0 to 6.0 N/m with a scan speed of 0.7 line/sec and scan area of $10 \times 10\,\mu m^2$. Scanned images were analysed using SPIP software (Surface Imaging Systems, Herzogenrath, Germany).

3. Results and discussion

3.1. Variations of the chemical surface heterogeneity with respect to pH

Zeta potential of ESPA2 as a function of pH was determined to assess the surface chemical characteristics and displayed in Fig. 1(a). Results show that ESPA2 has an isoelectric point (IEP) between pH 3.5 and 4.5. ESPA2 is positively charged at low pH and becomes negatively charged as increasing pH. X-ray

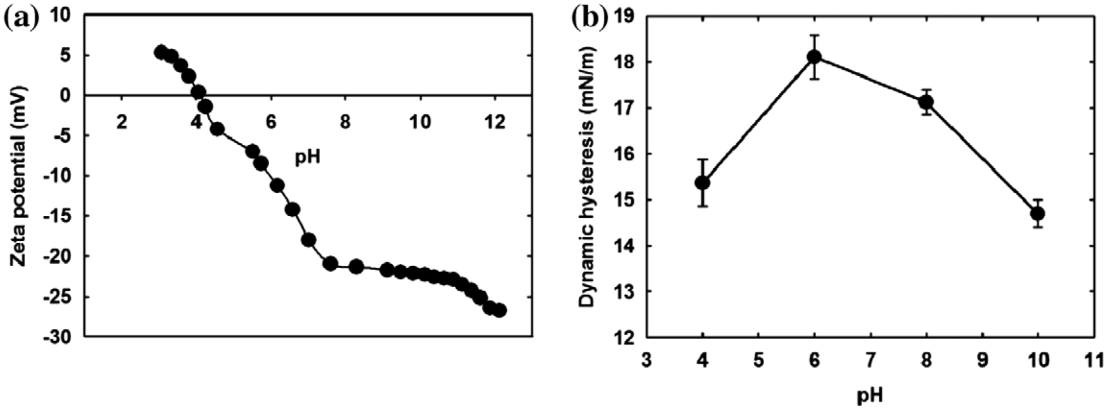

Fig. 1. Characteristics of ESPA2 membrane as a function of solution pH: (a) zeta potential and (b) dynamic hysteresis.

photoelectron spectroscopy and Fourier transform infrared spectroscopy analyses also suggest that most RO membranes contain carboxylic acid, amine and amide functional groups and have negatively and positively charged sites [23]. Dynamic hysteresis was measured from pH 4 to pH 10 under the ionic strength of 10 mM. Dynamic hysteresis increased from pH 4 to 6, but started to decrease above pH 6. Measured dynamic hysteresis shown in Fig. 1(b) corresponded well to zeta potential as chemical surface heterogeneity is closely related to the deprotonation of functional groups on the surface [20]. When the IEP of the membrane is approached, positively charged functional groups disappear and impart to the membrane surface a net neutral charge. Therefore, dynamic hysteresis decreases as the membrane surface turned to be homogeneous in terms of surface charge distribution. Above the IEP, the negative functional groups increased, making the surface charge partially negative. Thus, dynamic hysteresis increased due to relatively heterogeneous charge. As the pH increased further, the surface functional groups continued this process until the membrane surface became fully deprotonated at high pH, making it chemically homogeneous with all sites being negatively charged. As a result, dynamic hysteresis became the lowest value due to the chemically homogeneous surface. These results imply that dynamic hysteresis is a good measure of assessing the chemical surface heterogeneity of RO membranes.

3.2. Variations of chemical surface heterogeneity with respect to ionic strength

It has been well known that zeta potential could not be measured under high ionic strength such as seawater TDS conditions. However, dynamic hysteresis can be measured under such a high ionic strength. Dynamic hysteresis of ESPA2 membrane was determined under various ionic strength conditions at the fixed pH of 8.0 and the results are shown in Fig. 2. The significant change of dynamic hysteresis was observed. As ionic strength increased from 10 mM to 0.2 M, dynamic hysteresis also increased. This increase is attributed to the fact that some of charged sites (note that the solution pH is 8.0) lost their charges due to charge screening effect. Above the ionic strength of 0.2 M, however, dynamic hysteresis values decreased significantly until ionic strength reached to 0.4 M. This implies that most of charged sites lost their charge characters (i.e. all the sites were fully screened by surrounding salts).

It is well known that the membrane charge diminishes with increasing the ionic strength of background electrolyte due to charge screening. Consequently, chemical heterogeneity of the membrane surface increases due to heterogeneous distribution. This is conceptually illustrated in Fig. 3. Above ionic strength of 0.2 M, the negative charges on the membrane

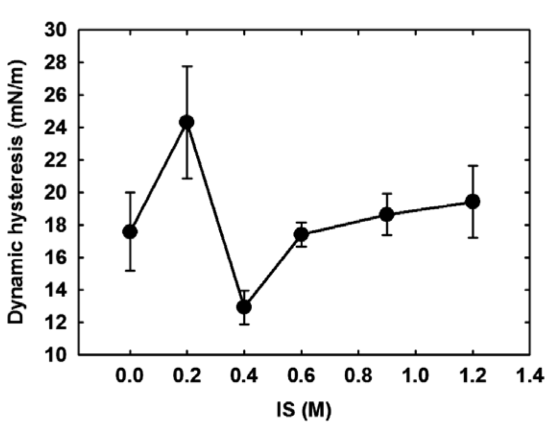

Fig. 2. Variation of dynamic hysteresis of ESPA2 with respect to solution ionic strength under pH 8.

surface continued to be screened, imparting to the membrane surface a net neutral charge. As the ionic strength of feed water increased further, the membrane surface became fully screened at high ionic strength, making it chemically homogeneous with all sites. However, after the membrane surface became fully screened, dynamic hysteresis started to increase. The reason for the further increase in dynamic hysteresis above 0.4 M ionic strength is attributed to the fact that physical heterogeneity plays more important role than chemical heterogeneity at this high ionic strength since osmotic swelling at high ionic strength results in the increase of physical surface heterogeneity [24,25]. Therefore, the interplay between chemical and physical surface heterogeneity with respect to ionic strength is a key mechanism governing the alteration of dynamic hysteresis and, thus, membrane fouling in seawater desalination.

3.3. *Influence of divalent cations on the chemical surface heterogeneity and dynamic hysteresis*

Dynamic hysteresis of ESPA2 membrane was determined under pH 8 and the same total ionic strength conditions using monovalent cation (NaCl 0.2 M) and divalent cations ($CaCl_2$ 0.0667 M and $MgCl_2$ 0.0667 M) in order to evaluate the influence of divalent cations on the membrane surface heterogeneity. The results are shown in Fig. 4. Dynamic hysteresis measured under 0.2 M NaCl was 24.32 mN/m, while dynamic hysteresis measured under 0.0667 M $CaCl_2$ and 0.0667 M $MgCl_2$ were 15.72 and 15.36 mN/m, respectively. These results demonstrate that the influence of monovalent and divalent ions on dynamic hysteresis is different even at the same total ionic strength. It can be explained by the differences involved in the mechanisms of monovalent and divalent ions in diminishing charge of membrane surface. Monovalent cation can screen the surface charges without the change of the surface potential (i.e. no direct interaction with surface functional groups). On the other hand, divalent cations can affect the surface potential directly by binding with the surface functional groups. At the same total ionic strength, charge screening by divalent ions also occurs more significantly. Therefore, divalent cations affected the surface chemical property more than monovalent cation in spite of the same ionic strength. The results shown here are useful to estimate the influence of various salts on deviating membrane surface heterogeneity and, hence, the membrane fouling potential with different source waters.

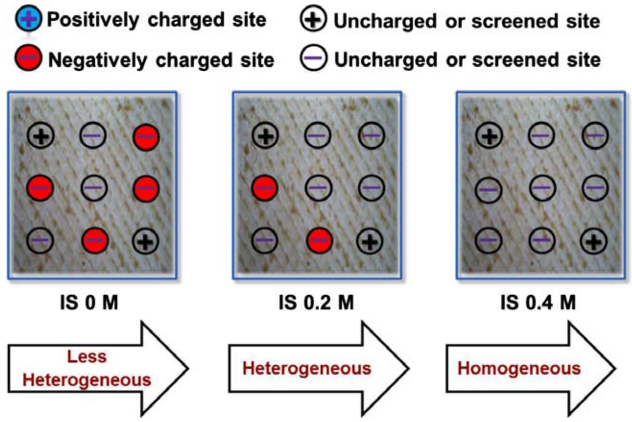

Fig. 3. Conceptual description of the changes in charge distribution of a heterogeneous surface with respect to solution ionic strength.

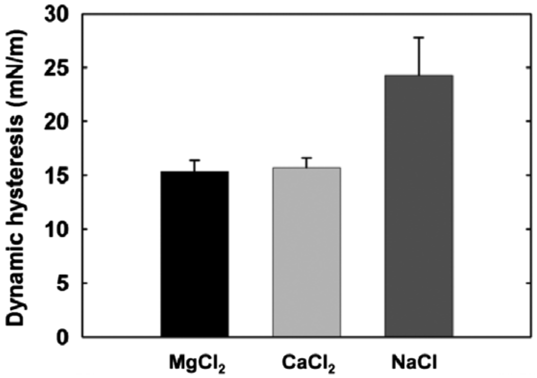

Fig. 4. Influence of monovalent (NaCl) and divalent ions (i.e. $CaCl_2$ and $MgCl_2$) on dynamic hysteresis under pH 8.

4. Conclusion

Variations of the chemical heterogeneity of RO membrane were investigated systematically by measuring dynamic hysteresis. The chemical heterogeneity of membrane surface was varied with respect to pH since the functional groups deprotonated with increasing pH. As the ionic strength increased from 0 to 0.2 M at pH 8, dynamic hysteresis increased, indicating more heterogeneous charge distribution. Above ionic strength of 0.2 M, however, dynamic hysteresis decreased significantly. These results indicate that the chemical heterogeneity was changed, since the membrane charge diminished with increasing ionic strength due to charge screening. At this high ionic strength similar to seawater level TDS, the chemical heterogeneity become negligible and play less important role in membrane fouling. However, with further increase in ionic strength, dynamic hysteresis values started to increase, since the membrane physical heterogeneity increased due to changes in surface roughness of polymeric thin films by osmotic swelling. Therefore, the interplay between chemical and physical surface heterogeneity should be considered for the accurate prediction of membrane fouling in seawater desalination. Influence of divalent cations on the surface chemical heterogeneity was also investigated and the results showed the divalent ions affected the chemical heterogeneity more than monovalent cations as divalent ions can directly interact with surface functional groups.

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