Surface chemical heterogeneity of polyamide RO membranes: Measurements and implications

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HIGHLIGHTS
• Chemical heterogeneity of RO membranes was first investigated using AFM.
• AFM probes were designed by employing negative CML and positive AAL colloids.
• Chemical heterogeneity was more pronounced with AAL probe than CML probe.
• RO membranes showed different charge distribution despite similar zeta potential.
• RO membrane with greater chemical heterogeneity was more prone to fouling.

GRAPHICAL ABSTRACT

ABSTRACT

The chemical heterogeneity (charge distribution) of polyamide reverse osmosis (RO) membrane surfaces and its influence on membrane fouling were investigated using atomic force microscopy (AFM). Negatively charged carboxyl modified latex (CML) and positively charged aliphatic amine latex (AAL) particles were employed to make AFM colloidal probes. The adhesive forces were significantly higher with the AAL probe due to negatively charged membrane surfaces. The chemical heterogeneity measured by AFM colloidal probes indicated that RO membranes could have chemically heterogeneous surfaces even if they exhibited similar average surface properties including zeta potential, contact angle and surface roughness. By performing fouling experiments with two commercial RO membranes of different chemical heterogeneities, it was demonstrated that RO membrane with high chemical heterogeneity was more prone to fouling, suggesting that surface charge distribution is one of the key factors governing RO membrane fouling. Consequently, surface chemical heterogeneity provides a new tool for accessing membrane fouling mechanisms and a novel concept for developing fouling resistant RO membranes.

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1. Introduction

Reverse osmosis (RO) and nanofiltration (NF) are adopted in a wide range of applications including seawater/brackish desalination, drinking water treatment, and wastewater reclamation [1–3]. Although the
RO membrane process becomes one of the most promising water treatment technologies, its efficient operation is often hampered by membrane fouling. Membrane fouling occurs when foulants are deposited and attached on membrane surfaces in a way that deteriorates membrane performance. The rate and extent of membrane fouling are greatly influenced by the surface characteristics of RO membranes, the solution chemistry of feed water, and the properties of foulants [4-10]. Of these influences on membrane fouling, membrane surface characteristics are generally the easiest to control since they can be altered during membrane manufacture. Thus, for reducing membrane fouling, the methods which characterize and modify membrane surfaces are practically significant.

Previous studies on particle transport and deposition processes showed that, to predict particle mobility in aquatic environments, theoretical deposition distribution rates calculated with electric double layer (EDL) theories could not be applied directly since particles tend to preferentially deposit onto specific collector surface locations [9,11-13]. Song et al. introduced surface charge heterogeneity using patch-wise and random distribution models, and suggested that the surfaces with small amounts of charge heterogeneity exhibited larger particle deposition rates than similar surfaces with no charge heterogeneity [11]. They also reported that changes in particle deposition rates over time were strongly influenced by the heterogeneity of porous media surfaces [12].

Until recently, only a few studies on the surface chemical heterogeneity of membranes have been performed despite its practical importance. The charge distribution of Poly (N, N-L-lysinediyterephthaloyl) microcapsule membranes was investigated under various feed pH and ionic strength using zeta potential measurements [14]. By identifying and mapping the functionality of membrane surfaces using atomic force microscopy (AFM), it was suggested that membrane surface chemical heterogeneities could affect colloid transport and attachment processes [15]. Kim et al. demonstrated that the propensity for bacterial adsorption and the related rate of biofilm formation were affected by membrane characteristics, and favorable sites for bacterial adhesion could exist on membrane surfaces due to surface heterogeneity [16]. Recent studies have shown that the chemical and physical heterogeneities of RO membranes could be investigated by dynamic hysteresis, allowing membrane surface heterogeneity to be measured quantitatively [17-19].

Zeta potential has been widely used for quantifying the magnitude of electrical charge at the double layer. However, the zeta potential only measures average membrane surface charge rather than its distribution [14,15]. Tirafere and Elimelech introduced two experimental methods to directly determine the concentration of negatively charged functional groups at the surface of dense polymeric membranes through a uranyl cation binding (UCB) technique and a Toluidine blue O (TBO) technique [20]. Another method to characterize surface charge is measuring electrostatic interaction using AFM [21]. By attaching various surrogate particles to the AFM cantilever tip, the adhesive interaction force between particle and membrane surface could be evaluated and related to fouling potential [5,8,22-24]. Many researchers have used negatively charged carboxyl modified latex (CML) particles to represent carboxylic functional groups which are the predominant functional groups in natural organic matter [5,8,23]. However, since RO membranes typically have a negatively charged surface, it is expected that adhesion forces are much more pronounced with positively charged colloidal probes than negatively charged ones. Therefore, we have attempted to determine the chemical heterogeneity of negatively charged RO membranes using a positively charged colloidal probe for the first time.

The objectives of this study are two-fold: (i) to investigate the chemical heterogeneity of the membrane surface by measuring the distribution of the adhesive forces between RO membranes and AFM colloidal probes (i.e., both carboxyl modified latex (CML) and aliphatic amine latex (AAL) particles) at different locations on the membrane surface and (ii) to evaluate the membrane fouling tendencies of two membranes with different chemical heterogeneities. The method to determine the charge distribution of RO membranes by measuring adhesive interaction forces using AFM with positively charged colloidal probes, as described in this study, may prove useful for improving the understanding of RO membrane fouling.

2. Materials and methods

2.1. RO membranes

‘T’ membrane (Toray, Japan) and ‘S’ membrane (Hydranautics, USA) were used for the AFM force measurements as well as fouling experiments. These membranes were thin film composite (TFC) polyamide membranes. For storage, the membranes were immersed in deionized (DI) water at 4 °C and the water was replaced regularly. All analyses in this study were carried out at room temperature and thus the membranes were prepared by immersion in 20–25 °C DI water for 2 hours.

2.2. Membrane surface characterization

2.2.1. Static contact angle

Contact angle measurements were performed with a goniometer (DM 500, Kyowa Interface Science, Japan). The equilibrium contact angle measurements described by Marmur were adopted [25]. The equilibrium contact angle was the average of the left and right contact angles and then the average of ten equilibrium contact angle measurements on different membrane coupons was reported.

2.2.2. Zeta potential

Membrane zeta potential was analyzed by a streaming current electrokinetic analyzer (SurPass, Anton Paar GmbH, Austria) following the procedure described by Luxbacher [26]. The zeta potential value was interpreted based on the Fairbrother and Mastin approach. For surface zeta potential analysis, 0.01 M KCl was used as background electrolyte solution, and the pH was varied from 2 to 10. Operating pressure ranged from 0 to 500 mbar and the temperature was about 25 °C. The zeta potential was measured three times and the average value was reported.

2.2.3. Surface roughness

Membrane surface roughness was analyzed by AFM imaging (PUCOStation AFM, Surface Imaging Systems, Germany). Liquid phase AFM imaging was conducted in contact mode with silicon probes (APPNANO, Applied Nano Structures Inc., USA). Root mean square (RMS) roughness was measured following the procedures described in previous studies [5,6]. All membranes were scanned three times, and each time the scan position was randomly selected.

2.2.4. Dynamic hysteresis

Dynamic hysteresis was determined using the Wilhelmy plate method [27] and measurements were carried out using a Sigma 701 microbalance (KSV Instrument Ltd., Finland) interfaced with a PC for automatic control and data acquisition. During the measurements, the membrane sample was held vertically attached to a microbalance, and a cell of test liquid moved up and down repeatedly at a constant speed. All the parameters followed during the hysteresis measurements are given by Lee et al. [17]. The surface tensions of the test liquids were measured each time by the Force Du Nouy ring method at test liquid temperatures between 20–24 °C and humidity between 20–25%. The ring was rinsed with ethyl alcohol and cleaned by burning it in red hot flame of a Bunsen burner prior to each measurement.

2.3. AFM force measurements

Colloidal probes were made by attaching an aliphatic amine latex (AAL) particle or a carboxyl modified latex (CML) particle (Interfacial Dynamics Corp., USA) with Norland optical adhesive (Norland products Inc., USA) to an AFM tip-less cantilever. According to the information
provided by the manufacturer, both AAL and CML particles have a nominal diameter of 4 μm. Force measurements were performed in contact mode with SiN probes, the back of which have a gold reflex coating for better resolution and stability in liquid phase applications (APPNANO, Applied Nano Structures Inc., USA). The probes have a spring constant of 0.1 N/m (±0.08 N/m), resonance frequency of 28 kHz (±10 kHz), and cantilever length of 225 μm (±10 μm).

The attachment procedure described in previous studies [5,8] was carried out on a micromanipulator and monitored in real time through microscopy. Particles were dropped on a cleaned mica surface and dried in a desicator. Using the micromanipulator, small doses of glue were spread on the mica surface covers at the end of the tip-less cantilever, and then a single sphere was picked up. After attaching the particle, the colloidal probe was cured under UV light (320–400 nm) for 30 min. The microscope image of the hand-made colloidal probe is shown in Fig. 1.

The experimental protocol for measuring the adhesive interaction force was based on the method described in previous studies [8,28]. The total measurement area was 30 μm × 30 μm, but it was subdivided into nine 10 μm × 10 μm sections to investigate the distribution of the adhesive interaction forces. To assess adhesive interaction force by membrane–particle interaction, only the retracting force curves were used and they were processed with SPIP software (Surface Imaging Systems, Germany) to obtain the force versus surface-to-surface separation curves. The adhesion force was obtained by multiplying the deflection of the colloidal probe with its spring constant. At least 15 measurements were taken at each section, and the average of their corresponding force values was reported. The test solution was 10 mM NaCl at pH 7 and had a temperature of 25 ± 1 °C.

2.4. Lab-scale RO fouling experiments

Alginic and humic acid (Sigma-Aldrich, USA), received in powder form, were used as model organic foulants. Stock solutions (2 g/L) were prepared by dissolving each foulant in deionized (DI) water, followed by filtration with a 0.45 μm filter (Millipore, USA), and then stored in sterilized glass bottles at 4 °C. For all of the RO fouling tests, the feed water composition was identical in terms of foulant concentration, pH, ionic strength, and temperature. The concentrations of alginate and humic acid were respectively fixed at 500 mg/L and 200 mg/L to accelerate membrane fouling. The pH, total ionic strength, and solution temperature were kept at 7, 10 mM, and 20 °C, respectively. The ionic strength of the solutions was controlled by NaCl (Junsei Chemical, Japan). NaCl was added to DI water and was mixed for 1 h at room temperature (20–25 °C). When needed, the pH was adjusted with 0.1 M NaOH or HCl. All test solutions were freshly prepared 1 h before each experiment and disposed of after the experiments.

A laboratory-scale cross-flow RO membrane test unit, similar to that described in other publications [4,6,8], was used for the fouling experiments. The rectangular plate-frame cell was 14.6 cm long, 9.5 cm wide, and 0.2 cm high. The system was operated in closed-loop mode with both permeate and concentrate being recirculated into the feed water reservoir. Permeate flux was continuously monitored using a digital balance and recorded in real time with a laboratory computer. The fouling experiments were conducted at an initial flux of 12.75 μm/s and a pressure of 2 MPa for a total operating time of 300 min.

3. Results and discussion

3.1. Surface characterization of RO membranes

In order to investigate surface charge distribution more accurately, typical surface properties of the RO membranes used in this study were first evaluated in terms of zeta potential, contact angle and roughness (Table 1). The contact angles of ‘T’ and ‘S’ membranes were 79.0° (±5.2°) and 72.4° (±4.9°), respectively. The RMS of membrane roughness was measured at 91.5 nm (±9.2 nm) and 97.0 nm (±11.8 nm), for ‘T’ and ‘S’ membranes respectively. These results might indicate that the ‘S’ membrane was slightly more hydrophilic and physically rougher than the ‘T’ membrane since the increased surface of a hydrophilic substrate makes the membrane surface more hydrophilic. However, the effect of hydrophilicity and surface morphology on surface heterogeneity could be neglected since both contact angle and surface roughness of these two RO membranes were close to or within the range of error.

The zeta potential of RO membranes was measured as a function of solution pH and shown in Fig. 2. The results showed that both membranes were positively charged below an isoelectric point (IEP) near pH 4 and became negatively charged at a pH over IEP, implying that the membrane surface consisted of various functional groups such as carboxylic acid, amine, and amide [29]. The positively charged surface when pH was below the IEP was attributed to the protonation of amine functional groups, while the negatively charged surface when pH was over the IEP was ascribed to the deprotonation of the carboxyl functional groups [30]. From this observation, it can be concluded that RO membranes contained negative charges on their surface at neutral pH, but also a lesser number of positive ones as well.

3.2. Protocol for measuring the surface charge distribution of RO membranes

To investigate membrane surface charge distribution, AFM force measurements were performed using CML particles which are negatively charged due to their carboxylate functional groups, fully protonated under the experimental conditions [31]. The deflection–distance curves, shown in Fig. 3(a), were obtained during each force measurement, and converted to the adhesive interaction forces as presented in Fig. 3(b) using the cantilever spring constant [8]. The ‘S’ membrane exhibited stronger adhesive interaction forces than the ‘T’ membrane. Both membranes displayed quite weak adhesive interaction forces although repulsive forces were expected because both CML particle and membrane surface were negatively charged under the experimental conditions. The presence of this adhesive interaction force may imply that RO membrane could have positively charged sites.

In addition to CML particles, AAL particles were adopted as colloidal probes since the AAL particle is highly positively charged at pH 7. The

![Attached colloidal particle](image_url)

**Fig. 1.** Microscope image of the AFM colloidal probe attaching to a particle.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle (°)</th>
<th>Zeta potential (mV)</th>
<th>Roughness (nm)</th>
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<tbody>
<tr>
<td>‘T’ membrane</td>
<td>79.0 (±5.2)</td>
<td>-18.3 (±2.2)</td>
<td>91.5 (±9.2)</td>
</tr>
<tr>
<td>‘S’ membrane</td>
<td>72.4 (±4.9)</td>
<td>-21.2 (±1.6)</td>
<td>97.0 (±11.8)</td>
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*Zeta potential was determined with a background electrolyte solution of 10 mM KCl.
deflection-distance curves (Fig. 4(a)) were converted to adhesive interaction forces using the cantilever spring constant (Fig. 4(b)). The results implied that the AAL probe may be more useful than the CML probe for investigating charge distribution since it produced significantly higher adhesive interaction forces. The AAL particles possessed positive charges which induced stronger electrostatic attraction forces with the negatively charged RO membrane surface. As a result, the adhesive interaction forces increased significantly for both membranes. The difference of adhesive interaction forces between both membranes also increased remarkably from 1.12 nN to 9.46 nN as indicated in Figs. 3(b) and 4(b). Furthermore, these observations inferred that positively and negatively charged sites may exist on the membrane surface, and thus both negatively charged CML and positively charged AAL particles should be used simultaneously when investigating surface chemical heterogeneity.

3.3. Charge distribution of RO membranes

The adhesive interaction forces were measured on nine sections of the RO membrane surface using negatively charged CML and positively charged AAL particles to determine surface charge distribution. The results summarized in Fig. 5 clearly demonstrated that the overall adhesive interaction forces of ‘S’ membrane were larger than those of ‘T’ membrane. The RO membranes also showed heterogeneously distributed patterns of adhesive interaction forces. When comparing the adhesive interaction force distributions of the two membranes, it seems that the ‘S’ membrane has a more heterogeneously charged surface than the ‘T’ membrane. However, it is hard to distinguish their surface chemical heterogeneity more precisely. Thus, a more quantitative approach is needed for measuring surface chemical heterogeneity.
In order to quantify the distribution of adhesive interaction forces, a standard deviation of adhesive interaction forces was considered first. A low standard deviation indicates that data points tend to be very close to the mean, whereas a high one designates that they are spread out over a large range around it. The standard deviation of average adhesive interaction forces for each section was calculated and the results are presented in Fig. 6. The standard deviations of ‘S’ membranes were larger than those of ‘T’ membranes, indicating that the ‘S’ membrane had more heterogeneous charge distributions than the ‘T’ membrane. Relative standard deviation was also considered as a metric for quantifying the surface chemical heterogeneity more meaningfully, and was estimated by dividing the standard deviation by the average adhesive interaction force. When using the CML particles, the relative standard deviations of ‘S’ and ‘T’ membranes were 0.735 and 0.743, respectively. However, when using the AAL particles, they were 0.375 and 0.57. These results may suggest that the ‘T’ membrane exhibited higher positive and negative chemical heterogeneity than the ‘S’ membrane.

The patch-wise model, developed for predicting particle deposition rates on heterogeneously charged surfaces in porous media, suggested that the total particle deposition rate is a sum of the local particle deposition rates on all the favorable and unfavorable patches [11,32]. Similarly, the fouling on different membrane surface patches is expected to be additive, and so when their variation is large, the patches with the highest attraction forces may dominate and determine the rate and extent of fouling. From this discussion, it can be stated that absolute standard deviation of adhesive interaction forces is an appropriate measure to represent chemical heterogeneity particularly when membrane fouling is analyzed.

### 3.4. Influence of charge distribution on membrane fouling

Bench-scale fouling tests were performed to investigate the influence of charge distribution on the fouling propensities of RO membranes. The resulting flux decline curves are shown in Fig. 7. Alginate was employed as a model foulant representing polysaccharide, and the high concentration of 500 mg/L was used to accelerate fouling [5,17]. Humic acid was also used as another model foulant representing...
natural organic matter (NOM), and its concentration was set at 200 mg/L. The experimental results showed that the ‘S’ membrane exhibited higher flux decline than the ‘T’ membrane with both foulants (Table 2). Thus, it may be delineated that RO membranes with heterogeneous charge distributions are more prone to fouling.

Other surface characteristics affecting membrane fouling should also be considered in order to confirm that surface charge heterogeneity is a key factor affecting membrane fouling. As shown in Table 1, the contact angle and RMS roughness of these two membranes were close to or within the range of error, suggesting that the effects of hydrophilicity and surface morphology on the difference in flux decline of these membranes could be negligible. Regarding the zeta potential, it was expected that, due to its higher zeta potential, the ‘S’ membrane would have a weaker fouling propensity than the ‘T’ membrane [7]. However this expectation was not met by the measured fouling tendency shown in Fig. 7. This implies that when predicting membrane fouling, not only should the zeta potential, an indication of average surface charge, be considered, but also the charge distribution.

Lee et al. introduced the concept of dynamic hysteresis as a useful tool for determining the surface chemical heterogeneity of the SWRO membrane [17]. Dynamic hysteresis (DH) represents the difference between the forces applied to a membrane surface when it is advanced into and withdrawn from a liquid or solution. A high DH value means that the membrane has a chemically heterogeneous membrane surface. The measured dynamic hystereses of the ‘S’ and ‘T’ membranes were 28.6 (±1.93) mN/m and 24.19 (±1.09) mN/m as summarized in Table 2. Dynamic hysteresis was correlated with the standard deviation of adhesive interaction forces and thus with fouling tendency. Therefore, when analyzing in accordance with the patchwise model, it can be concluded that the ‘S’ membrane has more favorable sites for membrane fouling than the ‘T’ membrane due to a more heterogeneous charge distribution. Consequently, foulants are easily adsorbed on the ‘S’ membrane surface since it has a higher area of favorable patches as shown in Fig. 8, resulting in severe membrane fouling. Similar observations were reported for bacterial adsorption due to membrane surface heterogeneity [16].

Lastly, it should be mentioned that only two RO membranes were examined in this study, primarily due to the difficulty in finding more than three membranes which have similar average surface properties but with different levels of chemical heterogeneity. Therefore,

![Fig. 7: Flux decline as a function of time (min). Fouling experiments were performed with (a) 500 mg/L alginate and (b) 200 mg/L humic acid. Experimental conditions: initial flux of 15.75 μm/s, cross-flow velocity of 8.5 cm/s, temperature of 20 °C, and 10 mM NaCl background electrolyte.](image)

![Fig. 8: Conceptual description of the influence of patch-wise heterogeneous surfaces on foulant deposition: (a) chemically heterogeneous surface (‘S’ membrane) and (b) chemically homogeneous surface (‘T’ membrane). The favorable site represents the section where foulants are readily deposited (i.e., sites favorable for deposition) due to positively charged characteristics. Despite similar surface charge properties (e.g., average zeta potential), the ‘S’ membrane exhibited a more chemically heterogeneous surface than the ‘T’ membrane due to the difference of their charge distributions.](image)

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<th>‘T’ membrane</th>
<th>‘S’ membrane</th>
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<tr>
<td>Dynamic hysteresis (mN/m)</td>
<td>24.19 (±1.09)</td>
<td>28.6 (±1.93)</td>
</tr>
<tr>
<td>Flux reduction for alginate (%)</td>
<td>30.98</td>
<td>38.58</td>
</tr>
<tr>
<td>Flux reduction for AHA (%)</td>
<td>3.95</td>
<td>7.28</td>
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* Dynamic hysteresis was measured at pH = 6.7–7.0 and a temperature of 20–25 °C.
* Flux reduction (%) was measured after 300 min.
additional research will be necessary to statistically associate chemical heterogeneity with membrane fouling propensity. Future study would be implemented by preparing RO membranes with varying degrees of chemical heterogeneity to systematically correlate chemical heterogeneity with membrane fouling. Furthermore, such an investigation could lead to the development of new fouling resistant membranes in the future.

4. Conclusions

In this study, the chemical heterogeneity of typical polyamide RO membrane surfaces was systematically investigated by measuring the adhesive interaction force distribution using AFM colloidal probes with negatively charged CML particles and positively charged AAL particles. The membrane fouling tendency of two RO membranes with different chemical heterogeneities was also examined to further elucidate the mechanism of RO membrane fouling. The primary findings drawn from this study are summarized briefly as follows:

- Adhesive interaction forces were significantly stronger with the positively charged AAL colloidal probe than the negatively charged CML colloidal probe since typical RO membranes were negatively charged.
- The charge distribution measured by AFM colloidal probes indicated that RO membranes had chemically heterogeneous surfaces.
- Standard deviation was used for the quantification of chemical heterogeneity and it could be related to membrane fouling propensity.
- The membrane with high surface chemical heterogeneity was more prone to fouling.
- The chemical heterogeneity provides a new insight for understanding RO fouling mechanisms, suggesting that membrane charge distribution is one of the key factors governing membrane fouling.

This study could have important implications for future effort to reduce membrane fouling by controlling the chemical heterogeneity of the RO membrane surface, which can lead to new development of fouling resistant RO membranes.

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