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Natural organic matter interactions with polyamide and polysulfone membranes: formation of conditioning film

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Abstract

A conditioning film changes the physicochemical properties of the membrane surface and strongly affects subsequent fouling behavior. Results from this Atomic Force Microscopy study indicate that Natural Organic Matter (NOM) characteristics, membrane surface properties, and solution chemistry are fundamental during conditioning film formation. Repulsive forces were observed between HUM (humic-NOM) and Polyamide (PA) or Polysulfone (PS) membranes during approach in Na^+ and Ca^{2+} solutions. However, repulsive and attractive forces were randomly recorded during BIOP (biopolymer-NOM) approach to both membranes, possibly caused by low electrostatic repulsion, hydrogen bonding, and presence of chemically/physically heterogeneous regions on membrane surfaces. During retracting, Ca^{2+} ions increased HUM adhesion to PA and PS membrane, indicating cation bridging/complexation as dominant interacting mechanism for this isolate. BIOP adsorption on PS and PA membrane was stronger than HUM under similar solution conditions, where hydrogen bonding would play an important role. Additionally, irrespective of solution conditions, higher adhesion energy was recorded on PS than on PA membrane for both NOM isolates, indicating membrane hydrophobicity as an important interacting factor. Results from this research will advance our understanding of conditioning film formation for NOM isolates and membranes of different physicochemical characteristics.

1. INTRODUCTION

Water quality and quantity are essential for the sustainability of every ecosystem. People rely on water for diverse activities (e.g., industrial applications, household consumption, etc.). However, many regions in the world are experiencing shortcomings in water supply because of extensive water demand, consequently exacerbating environmental problems [1]. Membrane treatment-based technology (e.g., membrane bio-reactor, desalination) has quickly evolved and expanded worldwide in an attempt to face the current challenges of water scarcity, becoming a suitable alternative to reduce pressure on natural water resources and to improve water quality [2].

Despite extensive research and recent breakthrough, membranes performance is still severely affected by fouling, resulting in increased energy consumption, operation costs, and short membrane life. A major foulant in membrane systems is natural organic matter (NOM) [3]. NOM (e.g., biopolymers, fulvic/humic compounds) is the complex and heterogeneous product of biological/chemical decay of living organisms. Although ubiquitous in aquatic environments, NOM characteristics can considerably vary from one water source to another [4, 5]. Previous research has provided a deep insight on NOM-fouling phenomena (e.g., membrane cross-flow systems, morphological analysis, membrane autopsy), suggesting that NOM characteristics, feed water, and membrane surface properties are influential during fouling [6-8]. However, the introduction of atomic force microscopy (AFM), colloidal probe technique, and chemical force microscopy (CFM) has signified a crucial advance in our understanding of a key aspect of fouling: conditioning film formation (i.e., interfacial NOM-membrane interactions). This conditioning film changes the physicochemical properties of the membrane surface and affects subsequent fouling behavior.

Previous AFM studies have focused on investigating this initial foulant deposition. For instance, hydrogen bonding was suggested as the main mechanism causing strong adhesion forces between hydroxyl-modified AFM probes and Polyvinylidene (PVDF) membranes (i.e., hydroxyl-modified and carboxyl-modified AFM probes have been widely used to simulate polysaccharides and humics, respectively) [9]. In a similar research, adhesion forces between carboxyl-modified latex (CML) probe and PVDF membrane decreased with increasing NaCl concentration [10], indicating influence of ionic strength on the interacting mechanisms. Likewise, adhesion forces between CML probe and Polyamide (PA) membrane in Ca^{2+} solutions were statistically distributed in a wide range, possibly due to membrane surface heterogeneities [11]. In addition, coating of AFM colloidal probes with model organic foulants has also been an important approach to study NOM-membrane interactions. Recent studies suggested hydrophobic effects as a dominant mechanism responsible for bovine serum albumin (BSA) strong adhesion to PVDF film or PA membranes [12, 13]. Interestingly, while bridging was the proposed mechanism between carboxyl groups on alginate and PA membranes in divalent cation solutions, low intermolecular and physicochemical interactions were observed between Suwannee River NOM and PA membranes [13]. Despite these recent research efforts, a comprehensive and comparative study of interactions between aquatic NOM isolates of different physicochemical characteristics and membranes as a function of solution chemistry has not been conducted and represents a key gap in knowledge.

In this investigation, a detailed methodology to study surface interactions between aquatic NOM and membranes is described. Gartempe River NOM and Brittany River NOM, both rigorously characterized in previous studies, were selected as model humic and biopolymer aquatic NOM isolates, respectively. Two manufactured membranes (PA and PS) were selected due to their

different properties. AFM was used as a sensitive technique that allows the study of specific and non-specific interactions at the interface [14]. Moreover, AFM can be adapted to closely mimic engineered water systems or aquatic environments by the measurement of interacting forces in solution of varied but controlled chemistry. The dominant mechanisms that govern NOM-membrane interactions as a function of their physicochemical characteristics and solution chemistry were proposed and correlated to the results of previous studies. The merit of this research is to advance our fundamental understanding of conditioning film formation during NOM-fouling, which would aid in the design and optimization of membrane coatings.

2. MATERIAL AND METHODS

2.1. Origin and characteristics of NOM isolates

The NOM isolates used in this investigation were collected from two surface water sources (Gartempe River and Brittany River, France) and then isolated following the protocol previously described [15]. Both fractions have been rigorously characterized in earlier studies [7, 16]. Gartempe River NOM (HUM) has been defined as a typical humic-like substance with a significant content of aromatic and phenolic carbon and high C/O, C/H, and C/N ratios. Fulvic structures and carboxyl groups are predominant. Conversely, Brittany River NOM (BIOP) is characterized by high nitrogen content and low content of aromatic/phenolic carbon. Amino sugars, proteins, and polysaccharides are found incorporated in BIOP structure, conferring it considerable hydrophilic properties. Although present, carboxyl groups are not the dominant functional group in BIOP. Also, BIOP is significantly less negatively charged than HUM [17].

2.2. Preparation of electrolyte solutions and NOM stocks

Analytical grade NaHCO_3 , NaCl , and CaCl_2 , and double-deionized water (DDI, 18 $\text{M}\Omega\text{-cm}$ resistivity, Millipore, USA) were used to prepare all the electrolyte solutions. These solutions

were filtered through a 0.22 μm sterile cellulose acetate membrane and stored at 4°C. NOM stocks were prepared by following the procedure described elsewhere [18]. Briefly, 20 mg of HUM or BIOP were dissolved in 100 mL of 1 mM NaHCO_3 solution, stirred overnight, and filtered through a 0.22 μm sterile CA membrane. The NOM stocks were then stored at 4°C in the dark. The total organic carbon (TOC) concentrations of the NOM stocks were measured with a TOC-V CPH total organic carbon analyzer (Shimadzu, Japan). Before use, electrolyte solutions and NOM stocks were sonicated and kept at 25°C. Iron oxide solution used for the modification of AFM colloidal probes (i.e., precipitation of iron oxide) was prepared by increasing the pH of a 10 mM FeCl_3 solution to 7 by small additions of NaOH as previously described [17].

2.3. Membrane selection and preparation

A polysulfone membrane (Dow Chemical, USA) and a thin-film composite (TFC) polymeric membrane with a polyamide surface layer (SWHR 30, Dow Chemical, USA), were selected for this investigation. Membranes were subjected to DDI water flux in a bench-scale cross flow system for cleaning purposes. Then, membranes samples were kept immersed in 0.22 μm -filtered 1 mM NaCl solution at 4°C until experimentation.

2.4. Membrane characterization

Contact Angle: The hydrophilicity of PA and PS membranes were characterized by contact angle measurement (Attension, KSV). The contact angle of each membrane sample was measured eight times using water droplet volumes of 5 μL . The values of contact angle were statistically processed by average and standard deviation analysis.

Streaming Potential: A SurPASS Electro-kinetic analyzer (Anton Paar, Austria) equipped with a flat-plate measuring cell (55 mm×25 mm) was used to measure streaming potential of PA and PS membranes. Experiments were conducted at unadjusted pH (5.8 ± 0.1) and at room temperature

using a target ramp pressure of 500 mbar. The ionic strength of the electrolyte solutions ranged from 1 to 100 mM for NaCl and CaCl₂. For each salt, new membrane samples were used. Four streaming potential measurements were collected and averaged for each solution condition.

Roughness of membrane surface by AFM in tapping mode: A 5500 Scanning probe microscope (5500 SPM, Agilent Technologies) was used to determine root mean squared surface roughness (R_{RMS}) and to generate topographic profiles of membrane samples by scanning their surfaces in tapping mode with a sharp silica AFM tip (k: 0.3 N/m, radius of curvature: ca. 10 nm, AppNano, USA). Membranes were fixed by a self-adhesive tape on the AFM stage and scanned over several 10 μm ×10 μm areas in 1 mM NaCl solution. Images were acquired in amplitude and height mode to provide both detailed topographic view and nm-scaled analysis.

Rutherford backscattering spectrometry (RBS) and Fourier transform infrared spectroscopy (FTIR): RBS was used to determine the elemental composition of PA and PS membranes. Protocols developed in previous studies were followed [19]. Briefly, characterization was conducted with a 2-MeV He⁺ beam of 3 nm in circular diameter. The membrane sample was positioned on a silicon wafer using double-sided tape and then placed on a holder in the vacuum chamber. The incident, exit, and scattering angles were set to 22.5°, 52.5°, and 150°, respectively. RBS spectrum (counts vs. energy) were acquired at different energy channels. Elemental composition of membranes was obtained by de-convolution analysis of the acquired spectra by SIMNRA software. The surface chemistry (i.e., presence of specific functional groups) of PA and PS membranes was analyzed by a PerkinElmer Spectrum 100 FTIR spectrometer equipped with a Universal ATR Sampling Accessory. A membrane coupon (1 cm×1 cm) was pressed between the ATR crystal and the plate after checking the contamination environment and background analysis. Five different locations on each coupon were analyzed

and 20 accumulations per signal spectra were recorded. An average spectrum was calculated for each coupon from the 100 profiles recorded. Each spectrum was acquired from 1300 cm^{-1} to 1800 cm^{-1} with a 4 cm^{-1} resolution.

2.5. Coating of AFM probes with NOM

A spherical silica particle of $10\text{ }\mu\text{m}$ in diameter (Polyscience, USA) glued to the tip of a cantilever (k : 0.06 N/m , AppNano, USA) was used as an AFM colloidal probe to minimize the topographical effect of rough polymeric membranes [14]. The modification of the colloidal probes was conducted by the layer-by-layer protocol using positively-charged iron oxide as an intermediate layer as previously described [17]. Briefly, the colloidal probes were immersed for 12 hours in a previously prepared iron oxide solution. After careful rinse in $0.22\text{ }\mu\text{m}$ pre-filtered DDI water, the iron oxide-coated AFM probe was immersed for 12 hours in a 1 mM NaHCO_3 solution containing HUM or BIOP at a final concentration of ca. 100 mg C/l . The NOM-coated colloidal probe was rinsed in DDI water and immediately used for AFM experimentation. A total of four HUM-coated AFM probes and four BIOP-coated AFM probes were simultaneously prepared for the following experimental conditions: a) PS membrane in 1 , 10 , and 100 mM NaCl , b) PS membrane in 0.33 , 3.33 , and 33.3 mM CaCl_2 , c) PA membrane in 1 , 10 , and 100 mM NaCl , and d) PA membrane in 0.33 , 3.33 , and 33.3 mM CaCl_2 solutions. In addition, another four HUM-coated AFM probes and four BIOP-coated AFM probes were prepared to conduct duplicates for reproducibility purposes. Micrographs of NOM-coated AFM probes before and after experimentation were performed on a Quanta 3D-FEG SEM (FEI, Netherlands) to assess the surface modification of the coated-probes as described elsewhere [17] (results not shown).

2.6. Interaction force measurement and data reduction

Force vs. distance profiles were acquired on a 5500 SPM (Agilent Technologies, USA) in contact mode. The spring constant of the cantilevers were measured before experiments by the thermal tuning method. Membrane samples were fixed by a self-adhesive tape on the stage of the AFM. Approaching and retracting force vs. distance curves were acquired at a 500 nm/s rate, i.e., consistent with previous studies [20], using Pico View v.1.8.2 software (Agilent Technologies, USA). The starting distance during approaching was set to 2 μm and the force load was carefully controlled to prevent damage of the NOM coating layer during interactions with membrane surface [14]. A minimum of 60 force curves were recorded at different locations of the membrane surface for every solution condition tested to conduct a comprehensive statistical analysis.

Every recorded force vs. distance profile was individually analyzed for: a) interaction force decay length and jump-in to contact events (i.e., occurring when the spring constant is exceeded by the gradient of the attractive forces) during approaching, and b) maximum adhesion force, maximum adhesion distance, and adhesion energy during retracting. Interaction force decay length (κ^{-1}) was calculated based on the repulsive forces following an exponential decay and were described by the equation: $F = F_0 \exp(-\kappa d)$ (i.e., F : interacting force, F_0 : force at contact, d : separation distance) [21]. Maximum adhesion forces and maximum adhesion distances were calculated as the maximum force and the maximum separation distance recorded before total NOM-coated probe detachment from the membrane surface, respectively. The adhesion forces were normalized to the radius of the colloidal probe [14]. Adhesion energies were calculated by integrating the adhesion forces with the separation distances using the trapezoidal rule as described elsewhere [22]. Nevertheless, a statistical approach was necessary to draw a

comprehensive picture on NOM/membrane interactions due to the physical/chemical heterogeneity of membrane surface and NOM isolates [23, 24]. Consequently, one single force profile could not be considered as representative of NOM/membranes interactions. Thus, adhesion energies, maximum adhesion forces and distances were processed by probability density functions where mean and variance were determined.

3. RESULTS AND DISCUSSION

3.1. Zeta potential of PS and PA membranes

The effect of solution chemistry on membrane surface charge was investigated by zeta potential analysis. Solution composition had a marked effect on the surface charge of both membranes. PS membrane displayed a more negative charge than PA membrane in solutions of low NaCl concentration (Fig. S1). This negative charge could be the result of the ionization of acidic functional groups. Double layer compression with increasing NaCl concentration was observed in both membranes [25]. In solutions of low CaCl_2 concentration, the charge of PA and PS membranes was significantly reduced by ca. 30 mV compared to that of NaCl solutions. With increasing CaCl_2 concentration, the zeta potential of both membranes closely approached to 0 mV. These results indicate a high Ca^{2+} ions impact on PA and PS membranes charge through cation complexation occurring on deprotonated carboxyl groups [26]. Previous studies have reported significant variability in zeta potential measurements for PA and PS membranes [26-28], suggesting a high influence of manufacture processes. However, zeta potential only provides bulk surface properties and does not deliver the nanoscale resolution of other techniques.

3.2. Morphology and roughness of membrane samples

Figure 1. Representative AFM images of a) polyamide and b) polysulfone membranes in 1 mM NaCl and at pH=5.8; T=20°C.

AFM images in tapping mode of PA and PS membrane provided a quantitative characterization of the surface roughness and revealed a complex morphology at the nanoscale (Fig. 1). Both membranes showed physically heterogeneous structures entirely consisting of peaks and valleys. The R_{RMS} of PA and PS membranes were calculated as 75.3 ± 5.6 nm and 61.5 ± 6.2 nm ($n=5$), respectively, and were consistent in magnitude to other commercial polymeric membranes [29]. Interestingly, membrane surface roughness has been suggested to strongly affect interfacial interactions (i.e., colloidal particles adhesion and even electrical double layer interactions) [30]. However, the similar R_{RMS} of these two membranes would aid in making a consistent comparison between NOM adhesion to PA and to PS membranes.

3.3. RBS, FTIR, contact angle, and elemental analysis

The energy spectrum of the PS membrane shows the signals of carbon, oxygen, and sulfur elements at approximately 0.5, 0.75, and 1.1 MeV, respectively (Fig. S2a). The energy of these plateau signals are directly correlated to the molecular weight of each element (i.e., carbon being the lightest while sulfur the heaviest). The signal of sulfur would be attributed to the presence of sulfone groups [19]. Conversely, the energy spectrum of the PA membrane (Fig. S2b) showed the signals of carbon, nitrogen, oxygen, sulfur, chlorine at approximately 0.5, 0.65, 0.75, 1.1, 1.3,

respectively. PA and PS membranes displayed major differences in elemental composition (Table S1), however, consistent with RBS results and their expected characteristics. Carbon was present in PS membrane in a more significant proportion. Sulfur was also observed, indicating the presence of sulfone groups. Conversely, nitrogen was detected in PA membrane in a considerable proportion, suggesting the presence of N-bearing functional groups (i.e., amides). FTIR spectra of PA membrane showed the presence of amide I, amide II, and aromatic amide on 1660, 1540, and 1609 cm^{-1} , respectively, all absent in PS membranes (Fig. S3). Elemental composition, RBS, and FTIR profiles provided important information regarding the presence of specific functional groups and elements abundance. Nevertheless, the accurate surface chemistry of both membranes (e.g., spatial distribution and accessibility of functional groups) is not known [31], consequently, adding a level of complexity to these systems. Additionally, PA and PS membranes have been previously demonstrated chemically and physically heterogeneous even at the nano-scale [25, 32]. The contact angles of PA and PS membranes were $57.8 \pm 1.9^\circ$ ($n=8$) and $67.2 \pm 2.9^\circ$ ($n=8$), respectively, indicating the higher hydrophilic character of PA membrane surface. These results are consistent to those of a previous comprehensive investigation reporting lower contact angles for several commercial PA membranes compared to PS membranes [33].

3.4. Interaction forces between HUM or BIOP and PA or PS membrane surfaces

Approaching and retracting force profiles provided crucial information about the range and type of interaction, and strength of adhesion between HUM or BIOP and PS or PA membranes.

Figure 2. Calculated decay length of HUM and BIOP as a function of NaCl and CaCl₂ concentration on a) polyamide and b) polysulfone membranes. Debye length was calculated by Classic DLVO theory and presented as dotted lines. Error bars depicts Standard Deviations.

Interactions during Approach: During HUM approaching to PA or PS membranes, long-ranged repulsive forces following an exponential decay, described by the concept of decay length [21], were observed at all solution conditions tested, irrespective of ionic strength and cation type. These decay lengths were statistically processed by average and standard deviation analysis as reported elsewhere [10]. Similarly, a previous investigation observed repulsive forces during approach between carboxyl-modified AFM colloidal probes (i.e., used as surrogates for humics) and polyethylene (PE) or PVDF membranes [9]. This result is consistent to that obtained in the current study, suggesting the importance of carboxyl groups on HUM during interactions with PS and PA membranes. Interestingly, few approaching curves randomly showed short-ranged repulsive forces (i.e., <4 nm separation distances) following a second exponential decay (bi-exponential) (Fig. S4a). These decay lengths (<1 nm) were not reported in this investigation.

The average decay lengths between PA membrane and HUM in NaCl and CaCl₂ solutions were statistically similar in magnitude (i.e., two tailed t-test, $p=0.05$) throughout the entire ionic strength range tested (Fig 2a). Although slightly higher in magnitude, the average decay length

between PS membrane and HUM (Fig. 2b) also showed independent of solution condition. By not following theoretical Debye length, these decay lengths indicate the presence of another dominant interacting force between the polymeric structures of membranes and HUM (i.e., of possible steric nature), besides electrostatics [21, 34]. Indeed, a high variability in the magnitude and range of double layer interactions has been previously measured among peaks and valleys of membrane surfaces, which contrasts from that of smooth surfaces (e.g., mica), indicating the influence of roughness on electrostatics [17, 30]. Also, HUM/membrane interactions contrasted with previously observed HUM/mica interactions [17], where ionic strength-dependent electrostatic forces were influential at long separation distances, while at a short separation distances the presence of steric forces from HUM polymeric structures were dominant. This result indicates the impact of membrane surface characteristics (e.g., polymeric nature/roughness) on its interactions with HUM.

In contrast, during BIOP approach to PA and PS membranes, two different kinds of interactions were randomly recorded: a) strong attractive forces with a gradient exceeding the spring constant of the cantilever causing “jump-in” to contact events (Fig. 4Sb), or b) repulsive forces following an exponential decay. These jump-in to contact events were observed in a significant number of the total generated force curves (i.e., ranging between 20%-30% and showing no clear trend or influence of ionic strength or ion valence) between BIOP and PA or PS membranes at every solution condition tested (Fig. 3). In a similar investigation, jump-in to contact events were recorded in every generated force profile between hydroxyl-modified AFM colloidal probes (i.e., used as surrogate for carbohydrate-like substances) and PE or PVDF membranes [9]. This previous study remarks the impact of hydroxyl groups during interactions with membranes.

However, unlike hydroxyl-modified AFM probes, BIOP is heterogeneous in structure and contains other functional groups in addition to hydroxyls (i.e., dominant in BIOP structure).

Figure 3. Probability of occurrence of jump-in to contact between BIOP and PA and PS membrane in NaCl and CaCl₂ solutions

This random occurrence of jump-in events or repulsive forces suggests that BIOP characteristics were influential during approach. The low charge, hydrophilicity, and high concentration of alcohol groups in BIOP structure would induce lower repulsive forces at both long and short separation distances during approach to membranes, than HUM. Additionally, the dominant presence of –OH in BIOP would cause short-ranged attractive forces due to hydrogen bonding with functional groups on membrane surfaces (e.g., deprotonated carboxyl, sulfone groups, etc.). In addition, the physical and chemical heterogeneities on both membranes would also contribute to this behavior. Chemical heterogeneities on the active layer, attributed to the interfacial polymerization manufacturing process, have been widely studied [24, 35]. For instance, the functional groups present on the active layer (i.e., producing pH dependent charges) are the result of incomplete polymerization and cross-linking [36, 37]. However, the concentration, accessibility, and type of functional groups (e.g., carboxylic, sulfone, or amine groups), and

degree of membrane cross-linking [38-40] are highly variable (i.e., heterogeneously distributed) and would impact BIOP-membrane interactions. Interestingly, commercial membranes of similar elemental composition, concentration of functional groups, and degree of polymerization have shown dissimilar ionization behavior and spatial distribution of functional groups [39].

Decay lengths between BIOP and PS or PA membranes (i.e., calculated when solely repulsive forces were recorded) were always higher than those of HUM, probably because of the longer polymeric structures of BIOP. Similarly to HUM, BIOP decay lengths were not visibly influenced by solution condition, thus, suggesting the presence of non-DLVO forces. The magnitudes of the decay lengths between BIOP and PA membranes were statistically similar at the ionic strength range tested (i.e., two tailed t-test, $p=0.05$). Decay length showing little variation with ionic strength has been previously reported between an AFM colloidal probe and polymeric membrane surfaces [10]. Interestingly, BIOP interactions with PA and PS membranes were also markedly different to BIOP/mica interactions (i.e., the latter solely showing strong attractive forces at short separation distances [17]), indicating the key influence of the membrane surface characteristics.

Interactions during Retraction: Retracting force profiles between HUM or BIOP and PS or PA membranes mostly showed multiple detachment events, which have been observed in previous studies and would be attributed to complex multiple discrete NOM adsorption on rough membrane surfaces [34]. The statistical analysis of maximum adhesion forces, adhesion distances, and adhesion energies was conducted by probability density functions due to scatter in the data possibly caused by physical and chemical heterogeneities on membrane surfaces [11, 13, 32]. This scatter in the data was not observed during BIOP or HUM interactions with mica in a previous study [17] due to the low roughness and chemical homogeneity of mica.

Figure 4. Mean values of: a) maximum adhesion force (mN/m), b) maximum adhesion distance (nm), and c) adhesion energies ($\times 10^{-18}$ J) in NaCl solutions.

Figure 5. Mean values of: a) maximum adhesion force (mN/m), b) maximum adhesion distance (nm), and c) adhesion energies ($\times 10^{-18}$ J) in CaCl_2 solutions.

HUM maximum adhesion forces to PA membrane increased from 1 to 10 mM NaCl, and then remained at a similar magnitude at 100 mM NaCl (i.e., 0.08, 0.17, and 0.18 mN/m, respectively) (Fig. 4a, S5), indicating an impact of ions on the adhesion mechanism. These adhesion forces were described by log-normal distributions, as similarly described between CML colloidal AFM probe and PA membrane in a previous investigation [41]. Adhesion distances and adhesion energies increased with increasing Na^+ concentration (Fig. 4b-c, S6-S7). Nevertheless, Ca^{2+} ions caused an impact on HUM/PA membrane interactions even at low concentrations. Maximum adhesion forces, adhesion distances, and adhesion energies at 0.33 mM CaCl_2 (0.26 mN/m, 27.7 nm, and 34×10^{-18} J, respectively) (Fig. 5a-c and S8-S10) were increased compared to those at 1 mM NaCl (0.08 mN/m, 11.3 nm, and 4.6×10^{-18} J, respectively). Additionally, the magnitude of these parameters also increased with increasing Ca^{2+} in solution. A cation bridging mechanism

would be occurring between deprotonated carboxyl groups on both HUM and PA membranes, which would be more efficient than simple charge screening caused by indifferent Na^+ ions as previously observed [42, 43]. Previous studies have reported this high affinity of humic-like materials towards PA membranes in the presence of divalent cations [44, 45]. On the other hand, BIOP maximum adhesion force, adhesion distances, and adhesion energies to PA membrane were higher than those of HUM in every NaCl condition tested (Fig. 4, S11-S13). This result indicates a higher affinity of BIOP to PA, possibly due to hydrogen bonding mechanisms involving hydroxyl groups on BIOP. The presence of Ca^{2+} ions also had an influence on maximum adhesion forces (Fig. 5, S14-S16). However, BIOP adhesion energies to PA membrane did not significantly vary with increasing Na^+ or Ca^{2+} in solution as opposed to HUM, indicating the importance of carboxyl groups on HUM structure during interactions with membranes.

HUM maximum adhesion forces, adhesion distances, and adhesion energies to PS membranes were practically insensitive to NaCl concentration in solution (Figure 4, S17-S19). However, in CaCl_2 solutions, HUM adhesion to PS membrane increased with Ca^{2+} concentration (Figure 5, S20-S22), therefore suggesting cation bridging/complexation as an important interacting mechanism for HUM. Additionally, HUM adhesion energies to PS were higher than to PA in Na^+ solutions, indicating the role of PS membrane properties during interactions. On the other hand, BIOP adhesion forces, distances, and energies to PS membrane were also similar in magnitude regardless of type and concentration of ions in solution (Figure 4-5, S23-S28). However, BIOP adhesion to PS membrane were always higher than those of HUM to PS membrane in both Na^+ and Ca^{2+} solutions. These results can be explained in terms of NOM and membrane characteristics as follows. In a previous study, stronger adhesion forces and adhesion

energies were measured between an hydroxyl-modified AFM probe and hydrophobic or hydrophilic membranes in NaCl solutions than with a carboxyl-modified AFM probe (i.e., used to represent non-humic and humics, respectively) [35]. This trend was also observed in the current study. Additionally, the lower adhesion energies measured between both NOM isolates and PA membrane compared to PS membrane were in good agreement with the lower adhesion energies measured between the functionalized probes and the hydrophilic membrane compared to the hydrophobic membrane [35]. Regarding PS membrane, sulfone confers membranes affinity for water (i.e., hydrophilicity) by making polymers polar (i.e., prone to hydrogen bonding). However, the presence of methyl groups ($-\text{CH}_3$) also grants non-polar characteristics to PS membranes, as previously suggested [33]. Previous investigations conducting AFM force measurements to self-assembled monolayers (SAM) reported higher adhesion of proteins and polysaccharides to hydrophobic $-\text{CH}_3$ groups than to hydrophilic $-\text{COO}^-$ or $-\text{OH}$ groups [46, 47]. This previous observation would indicate the importance of $-\text{CH}_3$ groups on PS membrane structure during interactions with HUM and BIOP. PS membranes are modified by the addition of PA active layers to provide strong ion rejection and high water permeability during desalination processes [48]. However, this PA active layer displays higher hydrophilicity than PS membranes (i.e., based on contact angle), and has been attributed to its surface functionalities [33]. The high hydrophilicity of amides discourages adsorption of organic substances by highly participating in hydrogen bonding [49]. Indeed, hydrogen bonds have been identified as a major connection between hydroxyl groups (i.e., dominantly present in BIOP) and membrane material [9], consequently explaining the high affinity of BIOP for PS and PA membranes, compared to that of HUM.

4. CONCLUSIONS

From the above described results, some key conclusions can be outlined:

- During approach, repulsive forces were recorded between HUM and PA or PS membranes in NaCl and CaCl₂ solutions. Electrostatic and steric repulsive forces between HUM (i.e., typical humic substances with a predominance of Fulvic acid structures and aromatic/phenolic carbon) and membrane polymer would cause this high repulsion.
- Attractive and repulsive forces were randomly recorded between BIOP (i.e., aliphatic in nature with a high concentration of alcoholic functional groups and weakly charged) and PS and PA membranes during approach. Low electrostatic repulsion, hydrogen bonding, and physical/chemical heterogeneities on membrane surfaces would induce this behavior.
- The presence of Ca²⁺ increased HUM adhesion forces, adhesion distances, and adhesion energies to PA and PS membranes, indicating cation bridging/complexation as an important interacting mechanism for HUM. Nevertheless, Ca²⁺ ions did not conclusively influenced BIOP adhesion to PS membrane.
- During retracting, higher adhesion forces and energies were observed between BIOP and PS or PA membranes than HUM at similar solution conditions. Hydrogen bonding would play a fundamental role during BIOP/membrane interactions as previously reported [9].
- BIOP and HUM adhesion to PS was higher than to PA membranes. The lower hydrophilicity of PS membranes (i.e., conferred by the presence of –CH₃ groups) would also play a crucial role during interactions.

In the current investigation, BIOP (hydrophilic NOM) have shown higher affinity to PA and PS membranes than HUM (hydrophobic NOM), indicating its importance during conditioning film formation. However, it should also be considered that in natural waters hydrophilic NOM only constitutes a small fraction of dissolved organic matter compared to humics. Results of this

investigation suggest that in addition to the NOM characteristics, the properties of the membrane surface are of fundamental importance during the conditioning film formation at early stages of fouling. In addition, these results indicate the importance of the selection of membranes in filtration systems to mitigate conditioning film formation during membrane fouling phenomena, and advances our fundamental understanding of NOM-membrane interactions at the interface as a function of their physicochemical characteristics.

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Highlights

- Humic NOM solely displayed repulsive forces to polyamide and polysulfone membranes
- Biopolymer NOM randomly displayed short-ranged attractive forces to membranes
- Ca^{2+} ions influenced adhesion of humic NOM to polyamide and polysulfone membranes
- Hydrogen bonding was a Biopolymer NOM dominant interacting mechanism with membranes
- Hydrophilicity of polyamide membrane was fundamental during NOM interactions