Effects of background cations on the fouling of polyethersulfone membranes by natural organic matter: Experimental and molecular modeling study

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Abstract

Adsorptive fouling of a polyethersulfone (PES) membrane by natural organic matter (NOM) in the presence of common metal cations was investigated with both experimental and computational molecular modeling techniques. NOM, calcium, magnesium and silicon were identified as important foulants through chemical analysis of two Midwestern surface waters. A model feed solution mimicking the lake waters and containing only NOM (Suwannee River NOM) and Ca\textsuperscript{2+} resulted in a fouling pattern similar to the surface waters; Mg\textsuperscript{2+} and Na\textsuperscript{+} caused much lower fouling at the same ionic strength as the calcium solution. Molecular modeling of the model solution allowed detailed probing of the fouling process. This work suggests that divalent ions (Ca\textsuperscript{2+} and Mg\textsuperscript{2+}) may cause membrane fouling not by forming “ionic bridges” between the negatively charged functional groups on membrane surface and the negatively charged functional groups of NOM, but by promoting the aggregation of NOM molecules in solution. The carboxyl groups of NOM strongly associate with the divalent ions, while the sulfonate groups in the polyethersulfone do not. Although Ca\textsuperscript{2+} and Mg\textsuperscript{2+} are both coordinated to the NOM carboxyl groups predominantly by outer-sphere-type complexation, Ca\textsuperscript{2+} associates with the carboxyl groups more strongly than Mg\textsuperscript{2+} due to the looser second hydration shell structure of Ca\textsuperscript{2+}. The stronger Ca\textsuperscript{2+}-NOM complexation is also manifested by the decreased mobility (diffusion coefficients) of the Ca\textsuperscript{2+} bound to the NOM.

Keywords: Ultrafiltration; Membrane fouling; Natural organic matter (NOM); Calcium; Molecular modeling

1. Introduction

Prediction of ultrafiltration performance is not generally possible without performing pilot-scale tests \cite{1,2} because membrane fouling is related to membrane material and solution chemistry \cite{1,3–9}. The inadequate understanding of membrane fouling has in many cases hindered wider adoption of membrane processes in large-scale drinking water treatment plants \cite{10}.

Several fouling mechanisms are described in the literature. Hydrodynamic forces exerted on particles and formation of cake layers have long been studied \cite{5,11–13}. Membrane modules for large-scale applications are designed in cross-flow configurations \cite{5,14}, and excessive cake formation can be controlled if filtration is performed under sub-critical-flux conditions \cite{15–17}. Filter deposits formed under these conditions tend to be easily removed yielding sustainable water productivity.

An often more-problematic flux loss is caused by adsorption of macromolecules on the membrane surface and in the membrane pores; this type of fouling can be especially important since drinking water supplies contain NOM \cite{18–22}. Hydrophobic membranes have long been considered more prone to the adsorptive fouling than hydrophilic membranes \cite{1,3,4}. Nevertheless, hydrophobic materials are still used because of their physical and chemical stability, and several studies have examined surface modification of hydrophobic membranes through additions of hydrophilic moieties \cite{23–25}.

Although NOM is considered as a major membrane foulant in drinking water treatment, the exact fouling mechanism is still debated. Researchers have attempted to determine if NOM hydrophobicity is related to fouling. Amberlite XAD-8 and XAD-4 resins \cite{26,27} have been used to separate and isolate...
the hydrophobic and hydrophilic portions of NOM, and examine the fouling characteristics of the fractions separately. While Nilson and DiGiano [28] claimed that the hydrophobic portion of NOM from the Tar river in North Carolina caused almost all fouling of a polysulfone NF membrane, Lee et al. [29] reported that the neutral hydrophilic fraction of NOM from river waters caused more fouling of various MF and UF membranes. Lee et al. [29] argued that the hydrophilic fraction, composed of polysaccharide-like colloidal matter, behaved very differently from the humic portion of NOM that is often assumed to be the primary foulant. The neutral hydrophilic portion of NOM was also implicated in fouling by Carroll et al. [30].

Contrasting experimental results and theories such as these indicate that the interactions between membrane surfaces and membrane foulants are not well understood. A more detailed picture of molecular interactions between membrane surfaces and NOM are required in order to better understand the fouling phenomenon.

Although the molecular structure of NOM is not very well defined, various acidic functional groups are generally present in NOM, and the concentration of carboxyl functional groups determines the organic acid characteristics of the NOM [31]. Thus, NOM is usually classified by its solubility in water at various pH values [32,33]. High ionic strength reduces the electrostatic double layer thicknesses of both membrane surface and NOM [34,35], which is believed to cause more severe membrane fouling [4,6,35]. In addition to the general ionic strength effect, the complexation of divalent ions (i.e., Ca^{2+} and Mg^{2+}) with acidic groups of NOM in natural waters has been considered to enhance fouling through NOM aggregation [4,6,36,37]. Ca^{2+} appears to interact more strongly with negatively charged carboxyl groups of NOM than Na^{+} and Mg^{2+} [38]. Binding of metal ions to acidic groups of NOM has been extensively studied [39–44] and quantitative models have been suggested [42,45–48]. Although researchers have observed that Ca^{2+} interacts stronger than Mg^{2+} with acidic functional groups, there is not yet an adequate explanation of why Ca^{2+} causes greater membrane fouling.

Computational molecular modeling techniques are successfully applied in the development of better molecular-level understanding of various properties and processes in modern chemical, biological, and materials sciences. They can be used to predict the structures and chemical interactions of biomolecules [49–53] and the behavior of polymer materials [54–56]. These computational modeling techniques have also been used to understand many membrane properties and processes on a fundamental molecular level [57–63]. In the present work, we applied molecular dynamics (MDs) computer simulations to model the processes related to adsorptive membrane fouling phenomena.

Although there can be no unique chemical structural model of NOM, several building blocks of humic substance structures have been proposed [64,65] and adopted in computational molecular modeling works [66–69]. Schulten and Schnitzer [64] suggested a polymeric humic acid structure with an elemental composition of C_{342}H_{388}O_{124}N_{12} and a molecular weight of 6651 Da. Pyrolysis-GC/MS, pyrolysis-FIMS, 13C NMR, electron microscopy, and several other analytic results were used to deduce this structure. Jansen et al. [65] proposed a three-dimensional structure, the so-called Temple-Northeastern-Birmingham (TNB) humic acid building block. The TNB structure had a chemical composition of C_{38}H_{39}O_{16}N with a molecular weight of 765 Da. The authors screened out unfeasible chiral isomers that could not result from biological transformations. This model was then successfully used in the conformational modeling study [70].

The interaction between NOM and metal ions in aqueous solutions has also been recently studied by molecular modeling techniques [66–69]. Sutton et al. [66] evaluated the hydration of the Schulten’s NOM model [64] and the interactions of Na^{+} and Ca^{2+} ions with the NOM molecule. They reported that calcium ions bind more strongly with NOM carboxylate groups than sodium, and that calcium yields better NOM hydration than sodium. It is thought that calcium better penetrates the NOM structure and creates more space for water molecules [66]. Xu et al. [67] combined NMR spectroscopy and MD modeling of an NOM-CsCl solution to show that Cs^{+} ions formed outer-sphere-type complexes with the NOM, while Cl^{-} ions did not interact with the NOM molecule. As a result, the diffusional mobility of the Cs^{+} ions decreased significantly, especially at low CsCl concentrations. The TNB model of NOM [65] was employed in these simulations because of its compositional similarity to the Suwannee River NOM (SRNOM) used in their experiments. The molecular weight of the TNB model [65] also seems consistent with recent studies suggesting that heterogeneous molecules, which have a molecular weight of about 500 Da, aggregate in aqueous solutions to form various supramolecular structures where hydrogen bonding between carboxyl groups and van der Waals forces between aromatic and aliphatic carbon structures hold the structure together [71–73]. Multications can increase apparent molecular weights of NOM through binding [74,75]. Recently, Kalinichev and Kirkpatrick [68] performed MD simulations to demonstrate that Ca^{2+} forms predominantly inner-sphere complexes with NOM, while the strong hydration shell of Mg^{2+} ions significantly decreases their ability to form even outer-sphere complexes with negatively charged functional groups of NOM. Deprotonated carboxyl groups were the major binding sites and the contribution of phenolic groups was negligible.

In this study, we investigated possible molecular mechanisms of membrane fouling by NOM in the presence of common metal cations. The main hypothesis at the outset of this work was that membrane fouling could be caused by cation binding of the partially negatively charged sulfonyl groups of the PES membrane and the deprotonated carboxyl groups of NOM molecules. The degree of binding can vary depending on the electrostatic charges and the sizes of the cations, because these parameters affect the ionic hydration structure and energy [68]. In order to quantitatively address the degree of binding interactions, membrane fouling by NOM was evaluated by both experiments and molecular modeling. Two Midwestern lake waters and Suwannee River NOM were used for the ultrafiltration experiments and the TNB molecular model [65] was adopted as a representative structure of NOM for the molecular dynamics simulations.
2. Experimental

2.1. Methods

2.1.1. Preparation of water samples

Two different Midwestern lake waters were directly sampled from the intake points of drinking water treatment plants. Lake Decatur water was collected from the South Water Treatment Facility at Decatur, Illinois. Lake Michigan water was collected from the Membrane Drinking Water Treatment plant in Kenosha, Wisconsin. The collected samples were stored in a 4 °C cold room to prevent microbial activity. A two-step pre-filtration, using a glass-fiber filter (AP40, Millipore, Billerica, Massachusetts) and a 0.45-µm hydrophilic nylon filter (Magna, GE Osmonics, Minnetonka, Minneapolis), was conducted to remove suspended solids from the feed water.

Freeze-dried powdered Suwannee River NOM (SRNOM) was purchased from the International Humic Substances Society (Lot number: 1R101N, St. Paul, Minneapolis). Powdered SRNOM was resolubilized in reagent-grade water to prepare a stock solution, which was diluted to 6 mg/L. The 6 mg of SRNOM was equivalent to 2.4 mg of carbon. Since the SRNOM solution contained fewer crude particles than the lake waters, removal of suspended solids was achieved in a single-step using a 0.45-µm hydrophilic nylon filter.

2.1.2. Ultrafiltration

A flat-sheet PES UF membrane with an average MWCO of 20,000 Da, was kindly supplied by the manufacturer, GE Osmonics (Minnetonka, Minneapolis). A dead-end, stirred-cell unit (Amicon Model 8050, Millipore, Billerica, Massachusetts) was used to evaluate water flux through the UF membrane. During filtration, the solution was continuously stirred at a fixed rotating speed of 275 rpm. Filtration was performed under a constant pressure of 105 ± 2.07 kPa, which was provided by a nitrogen gas cylinder. The filtration process consisted of five steps: wetting and cleaning the membrane, measuring clean water flux, filtering the NOM water sample, cleaning the membrane, and measuring clean water flux again. Forty milliliters of deionized water was then introduced into the cell and stirred without external pressure for 1 min for the cleaning. This step was repeated three times. Water flux was measured by weighing the permeate water over time with a digital balance (Model PB3002-S, Mettler-Toledo, Columbus, Ohio). Data from the digital balance were directly recorded using data-acquisition software (Winwedge Standard, TAL Technologies, Philadelphia, Pennsylvania). Temperature was adjusted to 294 ± 1 K by placement of a glass sample container in a continuously circulating water bath before the experiment.

2.1.3. Analysis

NOM was quantified as dissolved organic carbon (DOC), which was analyzed using a Phoenix 8000 TOC Analyzer (Tekmar-Dohrmann, Cincinnati, Ohio).

Metal analyses of the samples were conducted using the inductive coupled plasma (ICP) technique at the Illinois Water Survey’s (ISWS) Analytical Chemistry and Technology Unit in accordance with USEPA Method 200.7, Revision 4.4 (USEPA, 1994). The samples were preserved with 0.2% HNO3 (Fisher Optima High Purity Grade) immediately upon arrival in the laboratory. Samples were digested with 1% HNO3 and 0.5% HCl Optima acids in metal-free polypropylene sample tubes using a CPI ModBlockTM digestor. Digestates were analyzed for metals using a Thermo Jarrell Ash 61E ICP vacuum spectrometer with a fixed channel polychromator.

Chemical elemental compositions of the clean membrane and the fouled layers were analyzed by energy-dispersive spectroscopy (EDS) using an environmental scanning electron microscope (ESEM), Philips XL 30 ESEM-FEG (FEI Company, Hillsboro, Oregon). The membrane samples were dried in a desiccator for 5 days before analysis. 4-nm thick Au–Pd layer was sputter-coated in order to endow conductivity to the samples.

Chemical functional groups of membrane foulants collected on the surface of membranes were analyzed using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Nexus 670 spectrometer, Thermo Nicolet, Madison, Wisconsin). One liter of pre-filtered water sample was filtered through a 20-kDa PES membrane without stirring with the purpose of collecting an intact layer of foulants. The membrane was dried in a desiccator over 5 days before ATR-FTIR analysis. The membrane samples were cut into about 5 by 5 mm-sized squares and were pressed against the surface of zinc selenide (ZnSe) focusing element of an ATR accessory (Golden gate single reflection diamond ATR series ML II, Specac, Woodstock, Georgia). For each membrane sample, an averaged spectrum was obtained from a series of 32 scans.

2.2. Results

2.2.1. Lake water filtration

Water samples from Lake Michigan and Lake Decatur were also studied to simulate real drinking water supplies. Water flux changes and rejection of organic and inorganic constituents in the feed were monitored. The lake waters were filtered through 20-kDa PES membranes, which have been used in our lab for many studies of adsorptive membrane fouling [21,76,77]. Organic and inorganic constituents of feed and permeate waters were measured, and the membrane surface and fouled layer were analyzed. The analytical results were applied to formulate the SRNOM feed solutions when the concentrations of NOM and metal ions were set up.

Flux during filtration of Lake Michigan and Lake Decatur waters decreased by 37% and 48%, respectively, compared to initial flux values (Fig. 1). DOC rejection was low in both cases, 20% for Lake Michigan and 13% for Lake Decatur (Table 1). The standardized rinsing showed limited flux recovery at around 60% of the initial fluxes (Fig. 1). These results were typical of previous work with the same sources [76]. Twenty-nine inorganic elements in the feed and permeate were analyzed with ICP-MS. 4.4% and 2.7% of calcium in Michigan Lake and Lake Decatur waters were rejected by the membrane filtration. Magnesium showed no significant retention, which was in contradiction with the following EDS analysis (Table 1). Adsorption of Ca^{2+} on the polymer membrane surface has been previously observed [44].
The slight increase of sodium in the permeate water seemed to occur when Ca\(^{2+}\) replaced Na\(^{+}\) that had been captured in the polymer matrix via an ion-exchange type interaction. For Lake Decatur water, 5.8 mg/L of Si was detected in the feed and 13% of Si was rejected by the membrane. Particles retained on the glass-filter during the pre-filtration were analyzed with SEM, which identified clay particles and silicon-rich unicellular algae (diatoms). NOM and clay mineral debris are often considered to cause membrane fouling [76].

Chemical elements and functional groups of the fouled layers were analyzed with EDS and ATR-FTIR. As described in Section 2.1, to overcome detection limit problems, fouling layers were collected after filtering 1-L water samples through 20-kDa PES membranes. EDS analysis detected calcium and silicon in the fouled layers (Fig. 2). The detection of calcium and silicon in the fouled layers, and the rejection of these elements by the membrane, indicated that the two elements acted as membrane foulants. Strong peaks of carbon, oxygen, and sulfur resulted from the PES membrane itself. (Gold and palladium, which were used to coat the specimen, are also visible.) Silicon and calcium peaks were detected in the fouling layer of Lake Decatur water and a small calcium peak was detected in the Lake Michigan foulant. Therefore EDS and solution analyses show that NOM, silicon, calcium and magnesium were involved in the fouling process.

ATR-FTIR analysis expanded the picture of the fouling layers. The filtration of lake waters commonly resulted in the addition of carboxyl or amide groups to the clean membrane (Fig. 3). Corresponding peaks were detected at wavenumbers of 1540 and 1650 cm\(^{-1}\). Deprotonated carboxyl groups have two modes of vibration. Peaks arising from asymmetric stretching of \(\text{O}^+\text{C}=\text{O}\)–O– appear between 1540 and 1650 cm\(^{-1}\), while peaks from symmetric stretching appear between 1200 and 1300 cm\(^{-1}\) [78]. In addition, stretching of \(\text{O}^+\text{C}=\text{O}\) group near 1700 cm\(^{-1}\) and bending of \(-\text{C}=\text{O}\text{H}\) group between 1200 and 1300 cm\(^{-1}\) suggest the presence of protonated carboxyl groups [78]. Due to the similar structure of amide and deprotonated carboxyl groups, vibration frequencies are as well. Primary and secondary amide peaks are located at 1580 and 1650 cm\(^{-1}\), respectively [27,79]. Other common peaks were detected at 1130 and 1140 cm\(^{-1}\) for the filtration of lakes waters, which was assigned to polysaccharide-like material [79]. The silicon oxide bond (i.e., –Si–O) of clay minerals may also be apparent at 1080 cm\(^{-1}\) [76,80].

According to the filtrations and analyses, NOM, calcium, magnesium, and silicon seemed to be significant players in the fouling process. We formulated SRNOM feed solutions so the sum of individual metal ion concentrations yielded the same ionic strength as the Lake Michigan water. In this work, we excluded silicon in the model NOM filtration experiments and the molecular modeling in order to focus on the metal-NOM complexation.

### Table 1

Organic and inorganic contents of Michigan Lake and Lake Decatur waters

<table>
<thead>
<tr>
<th>Unit</th>
<th>SRNOM solution</th>
<th>Lake Michigan</th>
<th>Lake Michigan (20 kDa PES permeate)</th>
<th>Lake Decatur</th>
<th>Lake Decatur (20 kDa PES permeate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC mg/C/L</td>
<td>2.43 (0.60 permeate)</td>
<td>1.99</td>
<td>1.60</td>
<td>4.04</td>
<td>3.52</td>
</tr>
<tr>
<td>Fe mg/L</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Ca mg/L</td>
<td>&lt;0.18</td>
<td>36.50</td>
<td>34.89</td>
<td>48.02</td>
<td>46.72</td>
</tr>
<tr>
<td>Mg mg/L</td>
<td>&lt;0.05</td>
<td>12.35</td>
<td>11.87</td>
<td>18.22</td>
<td>18.79</td>
</tr>
<tr>
<td>Na mg/L</td>
<td>0.56</td>
<td>7.08</td>
<td>7.20</td>
<td>4.33</td>
<td>5.09</td>
</tr>
<tr>
<td>Al mg/L</td>
<td>&lt;0.13</td>
<td>&lt;0.13</td>
<td>&lt;0.13</td>
<td>0.03</td>
<td>&lt;0.13</td>
</tr>
<tr>
<td>Si mg/L</td>
<td>&lt;0.11</td>
<td>0.90</td>
<td>0.69</td>
<td>5.85</td>
<td>5.07</td>
</tr>
<tr>
<td>S mg/L</td>
<td>0.21</td>
<td>7.86</td>
<td>7.82</td>
<td>5.60</td>
<td>5.40</td>
</tr>
</tbody>
</table>

*Metal analyses were conducted at the Illinois Water Survey’s (ISWS) Analytical Chemistry and Technology Unit. According to the CCV values made from the same source as that used for calibration, 1.7–3.1% error was observed for a Ca standard measurement. Data presented in this table are averaged values of three measurements.*
membrane fouling. The Ca\textsuperscript{2+}-NOM solution showed the most severe membrane fouling with the nominal flux decrease exhibiting the fouling pattern (Fig. 1b) very similar to the ones observed for the lake waters samples (Fig. 1a). The Mg\textsuperscript{2+}-NOM solution resulted in a noticeably weaker fouling, while the Na\textsuperscript{+}-NOM solution did not cause any fouling at all (Fig. 1b).

The ionic strength of all metal-NOM solutions was set at 2.6 mM using the chloride salt of each metal in order to set each solution at the same electrostatic double layer thickness, while metal-free SRNOM had an ionic strength of 0.025 mM. The Ca\textsuperscript{2+} concentration was set at 35 mg/L following the Ca\textsuperscript{2+} concentration of the Lake Michigan water, while the concentrations of Mg\textsuperscript{2+} and Na\textsuperscript{+} were 21 and 61 mg/L, respectively. Since all three metal-containing solutions had the same ionic strength, the electrostatic double layer thickness (1/\(\kappa\)) in these solutions was assumed to be the same, calculated to be 59 Å according to the Debye–Hückel model:

\[
k^2 = \frac{e^2}{\varepsilon_0 k T} \sum_{i} z_i^2 n_i,\]

where \(e = 1.60219 \times 10^{-19}\) C is the electron charge; \(k = 1.38066 \times 10^{-23}\) J/K is the Boltzmann constant; \(\varepsilon_0 = 8.854 \times 10^{-14}\) C\(^2\)/cm/J is the dielectric permittivity in vacuum; and \(\varepsilon_{H_2O} = 80\) is the relative permittivity of water at \(T = 298\) K.

Different fouling patterns at the same ionic strength contrast with our original hypothesis, and clearly indicate that the fouling is not merely an ionic strength effect; rather it is suggested that ions having different charges bind chemical moieties of the membrane surface and/or NOM via a specific complexation. The divalent ions may form bridges between the membrane surface and NOM or simply cause aggregation of NOM molecules in solution. Although specific humic-metal complexations by divalent ions has been already suggested in membrane literature \([4,6,35,38]\), the different membrane fouling tendencies by Ca\textsuperscript{2+} and Mg\textsuperscript{2+} are not yet fully understood. Better knowledge of the dependency of complexation on the different ionic charges, sizes and ionic masses is necessary. The experimental investigation
of such atomic-level structural and dynamic properties of ions in aqueous solution is extremely difficult using current analytical methods. Therefore, we employed computational molecular modeling techniques to investigate detailed interactions between the metal ions and the functional groups of the membrane surface and NOM molecules.

3. Molecular modeling

3.1. Methods

3.1.1. Computational methods

MD computer simulations of atomic systems representing the hydrated membrane-NOM solution interfaces were performed using the Cerius-2 software package (version 4.9, Accelrys, San Diego, CA). Periodic boundary conditions were applied and a combination of the consistent valence force field, CVFF [81], and the recently developed CLAYFF force field [82] was used throughout the simulations to describe the interactions between all atoms. The simple point charge (SPC) water model [83] was used to describe the interatomic interactions of H₂O, and the recently developed CLAYFF force field [82] was used throughout the simulations to describe the interactions between all atoms. The simple point charge (SPC) water model [83] was used to describe the interatomic interactions of H₂O molecules with each other and with other components of the simulated systems. Ewald summation was applied to calculate long-range electrostatic interactions between atoms, while the “spline cut-off” method was used for the short-range non-electrostatic interactions [84]. The time step of 1 fs was used to numerically integrate the Newtonian equations of motion of all atoms. When the simulated systems reached their equilibrium states after a pre-equilibration period of ∼100 ps, the coordinates and velocities of all atoms along the simulated MD trajectory were periodically recorded every 10 fs for further statistical analysis.

Complexation of metal ions with the chemical moieties of the membrane surface and the NOM molecule was evaluated by calculating the radial distribution functions (RDFs), \( g_{ij}(r) \) and the running coordination numbers (RCNs), \( n_{ij}(r) \). RDF between a pair of atom types is defined as a normalized probability of finding atoms of one type, \( j \), at a distance \( r \) from the atoms of the another type, \( i \), in the simulated system. RCN, or the number of atoms of species \( j \) coordinating the reference atom of species \( i \) at a distance \( r \) can be calculated using Eq. (2) [84].

\[
n_{ij}(r) = 4\pi \rho_j \sum_{r_i} g_{ij}(r)r^2 dr
\]

where \( n_{ij} \) is the running coordination number of species \( j \) around species \( i \); \( \rho_j \) is the number density of species \( j \) in the system; \( g_{ij}(r) \) is the RDF between species \( j \) and species \( i \); \( r_{i,\text{max}} \) is a cut-off distance of the complexation in the calculation.

The degree of metal ion binding was also assessed by calculating the diffusion coefficients of the ions from their mean square displacements (MSDs) [84].

\[
D_i = \frac{\text{MSD}_i(t)}{6t} = \frac{\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle}{6t}
\]

where \( D_i \) is the diffusion coefficient of the species \( i \); \( \mathbf{r}(t) \) is the vector of atomic coordinates at time \( t \), and angular brackets denote the averaging over all species of type \( i \) present in the system and over all possible time origins along the MD trajectory, \( t = 0 \).

3.1.2. NOM model

The Temple-Northeastern-Birmingham (TNB) molecular model of humic acid [70] was adopted for our simulations because of its compositional similarity to SRNOM [67]. This molecule contains three carboxyl, two phenolic, and two amine groups representing the acidic property of humic acid and is consistent with the ATR-FTIR analysis discussed in Section 2. Considering a neutral ambient lake water pH, all three carboxyl groups of the model are assumed to be deprotonated, resulting in the total negative charge of ∼3. This negative charge was compensated by adding either of two divalent ions (i.e., \( \text{Ca}^{2+} \) or \( \text{Mg}^{2+} \)) and one \( \text{Cl}^- \) in order to maintain total charge neutrality. For the sodium system, four \( \text{Na}^+ \) ions and one \( \text{Cl}^- \) were added.

3.1.3. Construction of the simulation systems

A polyethersulfone (PES) polymer chain for the MD simulations was created out of 60 repeating monomer units using the “Polymer Builder” module of the Cerius 2 software [85]. This length can effectively represent polymer characteristics of polyethersulfone [86]. The chemical structure of the repeating monomer units is presented in the lower right side of Fig. 4a. One end of the chain was terminated with a hydrogen atom while the ether group at the other end was closed with a phenyl group.

Initially, the simulated polymer chain was enclosed in a large periodic box with dimensions 100 Å × 100 Å × 200 Å, resulting in a very low starting density of 0.0115 g/cm³. The polymer chain was then gradually “compacted” into progressively smaller periodic cells in order to form a new polymer having the required polymer density. Several cycles of energy minimization (EM) and MD simulations were repeated to allow the polymer chain to fold until the polymer structure had a density of 1.30 g/cm³, very close to the experimental density of PES which is 1.37 g/cm³ under ambient conditions [87]. After the first EM, an MD simulation was performed at a constant elevated pressure (0.1 GPa) and temperature (600 K) in the NPT statistical ensemble in order to speed up the process of folding of the polymer chain. An annealing MD simulation followed at the ambient conditions of 0.1 MPa and 300 K to release the torsional stresses of the polymer backbone. This process was repeated until the bulk polymer chain reached the desired density. Fig. 4 shows the final structure of the PES bulk polymer model. The described annealing process reduced the periodic box size of the folded bulk polymer structure down to 25.4 Å × 24.9 Å × 27.4 Å (Fig. 4b).

A model of an infinite PES surface was then created by cleaving the bulk PES polymer structure along the \( x-y \) plane using the “Surface Builder” module of the Cerius 2 software. All covalent bonds within the polymer chain were kept intact during the cleavage process, which created a natural roughness of the model membrane surface (Fig. 5). However, we did not make any attempts to model membrane pores in this study, focusing instead on the molecular-level details of the interactions between NOM, metal cations and the polymer surface. Upon cleavage, an
approximately 50-Å-thick empty space was added to the model along the $z$ direction (perpendicular to the surface) in order to make room for aqueous solution. A new periodic box was then made, which had the dimensions of $25.4 \, \text{Å} \times 24.9 \, \text{Å} \times 85.9 \, \text{Å}$, and included 1207 water molecules (Fig. 5a). The cycles of preliminary EM and MD simulations were repeated until the polymer became fully hydrated. For the first cycle of hydration, the positions of polymer atoms were fixed to prevent a
sudden deformation. The cycles were repeated until the system completely relaxed and reached an equilibrium state.

In order to model the membrane interface with aqueous NOM solutions, one TNB molecule [70] and metal ions (i.e., Na⁺, Mg²⁺, or Ca²⁺) were inserted into the previously created periodic box containing the hydrated PES membrane surface by replacing some H₂O molecules (Fig. 5b). Each model system was then equilibrated for 100 ps of MD simulation before the statistics of the structural and dynamic behavior of various species started to be accumulated over the equilibrium part of the MD trajectories. 300-ps long MD simulations were performed for each metal ion, except Na⁺, in order to evaluate the cation interaction with the PES membrane surface and the NOM molecule. In the Na⁺ case, the simulation was discontinued after 100 ps when the Na⁺ ion diffused out to the aqueous region between the polymer and the dissolved NOM.

3.2. Results

3.2.1. Hydrogen bonding and the molecular structure of the hydration layer at the water-PES membrane interface

The PES polymer has two characteristic alternating functional groups in its structure. One of them is a hydrophilic (sulfonyl) group and the other is a hydrophobic (benzene ring) (Fig. 4). Since the metal ions carry positive charge, fully or partially negative atomic moieties of the membrane surface can potentially interact with the ions electrostatically. The two oxygen atoms attached to a sulfur atom in the sulfonyl group of PES are the most probable interaction sites, each of which carry a charge of −0.3368e in the CVFF force field model.

Before adding metal ions and the NOM molecule to the system, we examined the interactions between water molecules and the membrane surface. A series of short 10-ps long MD simulations of PES membrane surface and water molecules were performed at constant volume and constant temperature \((T = 300 \, \text{K})\) conditions (NVT-ensemble) as preliminary control experiments. Hydrogen bonding between water molecules and the sulfonyl groups of the PES membrane surface was observed. The diffusive mobility of H₂O molecules near the PES surface was slowed due to hydrogen bonding between the water molecules and the oxygen atoms of the sulfonyl groups at the PES surface. The calculated diffusion coefficient of water molecules, from Eq. (3), near the PES surface was \(1.33 \times 10^{-5} \, \text{cm}^2/\text{s}\), compared with the bulk liquid water value of \(2.33 \times 10^{-5} \, \text{cm}^2/\text{s}\) under ambient conditions. The radial distribution function \(g(r)\) between oxygen atoms of the sulfonyl groups (o') and hydrogen atoms of H₂O molecules (h*) showed a typical hydrogen-bonding peak at a distances of around 2 Å. In contrast, the distances of the water hydrogens from the hydrophobic carbon atoms in the phenyl ring (cp) of PES were always much larger (Fig. 6). These results indicated that the sulfonyl groups of the PES polymer surface function as nucleophiles while phenyl rings do not show noticeably strong nucleophilic interactions with polar water molecules. We expected that similar type of electrostatic bonding may be formed between metal ions and the sulfonyl groups.

3.2.2. Metal cation association with PES membrane surface and NOM

The complexation of metal cations with the membrane surface and the TNB molecule was examined by analyzing the coordination of these ions to the possible complexation sites at the PES membrane surface (sulfonyl groups) and on the TNB molecular model (carboxylate and phenolic groups). It was observed that divalent Mg²⁺ and Ca²⁺ ions strongly associated with the carboxylate groups of the NOM molecule, while monovalent Na⁺ showed negligible association with TNB. In contrast, the sulfonyl groups at the PES membrane surface did not indicate any significant association with any of the metal ions. During the simulations, the metal ions were originally placed between the PES membrane surface and the TNB molecule for the MD simulations (Fig. 7) at an initial distance of ∼5 Å from the sulfonyl group of membrane surface and ∼6 Å from the carboxyl group of the NOM molecule. Initial distances of 2.5–8 Å between cations and each functional group were also tested. None of the cations showed any preference for association with the sulfonyl groups of the PES membrane surface over the 100-ps equilibration period or during the 300-ps equilibrium stages of the simulations. On average, the metal ions were typically located far from the oxygen atoms of the sulfonyl group—the RDFs showed a peak at around 7 Å. Na⁺ completely diffused out to the solution zone between the membrane surface and the NOM molecule very soon during the equilibration period (Fig. 8). During the MD simulations, the metal ions located between the PES membrane surface and the NOM molecule always preferred to move toward the NOM molecule and away from the membrane surface. For Ca²⁺, the free Brownian diffusion of the bound Ca²⁺ almost stopped as it approached and remained in the vicinity of the carboxylate groups during the simulation. Accordingly, since the relatively large TNB molecule moved much slower than the H₂O molecules and ions on the time scale of our simulations, the average distance between a cation and a surface sulfonyl group is approximately equal to the difference of two distances: the distance between the sulfonyl group of the membrane and the carboxylate group of the NOM molecule, and the distance of the metal ion from the carboxyl group of the NOM molecule. The RDFs shown in Figs. 8 and 9 demonstrate this relationship.
Electrostatic interactions between the charged sites of the PES membrane, cations, NOM and H$_2$O molecules in solution dominate the total interaction energy balance in our simulated systems and help to understand why the ions statistically prefer to stay hydrated by H$_2$O or to be associated with the NOM carboxylate groups, rather than to be adsorbed by the sulfonyl groups of the membrane surface. In our model, the sulfonyl groups carry a partial negative charge of $-0.3368e$ on each of their oxygen atoms, which is relatively smaller than that of the oxygen atom of a water molecule ($-0.82e$), and is even smaller than the negative charge carried by the oxygen atoms of the deprotonated carboxyl groups of NOM ($-0.57e$). Thus, the oxygen atoms of the sulfonyl groups seem not to have high enough partial negative charge to outcompete the H$_2$O molecules and NOM carboxylate groups for effective coordination of the metal ions.

The divalent cations in solution were strongly attracted to the carboxylate groups of NOM molecule, in contrast to their weak interaction with the membrane sulfonyl groups. The monovalent sodium ions showed negligible association with the NOM carboxylate groups due to their relatively small positive charge (Fig. 9). The average distance between the divalent ions and the oxygen atoms of the NOM carboxylate groups ranged from 4.3 to 5.7 Å, which is characteristic of outer-sphere metal-NOM complexation [68]. At the same time, sodium did not show a distinctive peak in this range of interatomic distances (Fig. 9).

Both Ca$^{2+}$ and Mg$^{2+}$ were coordinated predominantly by outer-sphere-type complexation to the NOM carboxylate groups, with the oxygen atoms of the carboxylate groups residing at approximately the same range of interatomic distances as the water molecules of the second hydration shells of these ions (Fig. 10). On average, the carboxylate groups had a greater chance of interacting with Ca$^{2+}$ than Mg$^{2+}$ due to the looser second hydration shell structure of Ca$^{2+}$. The eight nearest water molecules form the first hydration shell of Ca$^{2+}$ at $\sim$2.5 Å, while the second hydration shell is located around 5.0 Å from the ion, where, on average, one oxygen atom of the NOM carboxylate groups was also present in addition to water molecules (Figs. 10 and 11). On the other hand, six water molecules form a much more compact first hydration shell around Mg$^{2+}$ at a distance of $\sim$2.1 Å from the ion. Accordingly, the second hydration shell of Mg$^{2+}$ is also closer to the ion and more compact. Therefore, on average, only 0.6 oxygen atoms of the NOM carboxylate
groups can be found in the second hydration shell of Mg$^{2+}$ at the same distance of 5.0 Å.

Diffusion coefficients of cations were calculated according to Eq. (3) during the simulations (Table 2). The diffusion coefficients of divalent ions associated with the NOM carboxylate groups were much lower than the values for the hydrated ions in the bulk solution. Thus, the diffusion of Ca$^{2+}$ nearly stopped after 50 ps of simulation when the ion was associated with a carboxylate group. In contrast, the simulated diffusion coefficient of Na$^+$ was nearly unaffected by interaction with the NOM molecule.

### 4. Discussion

Oxygen atoms of the sulfonyl groups at the PES membrane surface are hydrophilic and can participate in hydrogen bonding interactions with surface water molecules, but their relatively low negative charge is shielded by hydration. Thus, the net interaction between the hydrated cations and the PES membrane surface remains weak and the cations do not interact strongly with the surface. However, it is still possible that another molecular mechanism, such as direct hydrophobic interaction between the membrane surface and NOM molecules, could also contribute to the total balance of membrane-NOM interactions. In the simulations, we could not observe any significant contribution of such hydrophobic interactions. However, the TNB NOM model used here is highly hydrophilic because the hydrophilic functional groups dominate its structure. Therefore, when this model is used, it is possible to miss subtle effects of the hydrophobic interactions; a complete evaluation would require much longer simulation times for much larger molecular models to allow for the dynamic alignment of the hydrophobic groups on the membrane surface with those of the NOM molecules.

Another possible pitfall is in the construction of the model membrane surface. Although a neutral PES membrane surface was employed here, actual membrane surfaces may contain charged moieties other than PES at ambient pH around 7 because the isoelectric point of the PES membrane, determined by zeta-potential measurements, is at around pH 2.2 [88]. Zeta-potential measurements indicate that most membrane surfaces have a negative charge [4,89], although this negative charge has been somewhat of a mystery since pure polymers are presumably used in other commercial membranes. There is a good deal of secrecy in the industry and end-users are usually not privy to the exact formulation of commercially available membranes. The other view is that the negative zeta-potential measurements are simply an artifact. It is possible that the high ionic strengths employed in zeta-potential measurements cause non-specific association of chloride with the membrane surface and pores [4,90].

Despite the fact that Ca$^{2+}$ ions consistently demonstrated in our simulations somewhat stronger association with the NOM carboxylate groups than Mg$^{2+}$ ions, in both cases this association occurred only in the form of outer-sphere complexes, with the oxygens of the carboxylate groups occupying on average only 5–10% of the second hydration shell of the ions and the hydrating water molecules occupying the rest. The consistent observation of outer-sphere-type complexation for both Ca$^{2+}$ and Mg$^{2+}$ indicates a relatively high energy barrier separating the hydrated states of the ions in solution and their states of direct inner-sphere association with negatively charged functional groups. On the other hand, Kalinichev and Kirkpatrick [68] have observed strong inner-sphere-type complexation for Ca$^{2+}$ and no complexation at all for Mg$^{2+}$ using the same model of NOM molecule in bulk aqueous NOM solutions. This behavior can be qualitatively explained in terms of the charge/size ratio for the ions. Due to the competition between ion hydration in bulk aqueous solution and adsorption of these cations by the negatively charged NOM carboxylate groups, larger ions of the same charge (e.g., Cs$^+$ vs. Na$^+$, or Ca$^{2+}$ vs. Mg$^{2+}$) have a stronger tendency for NOM association. At the same time, for ions of approximately the same size, higher charge results in a stronger association with NOM. Thus, in contrast to Mg$^{2+}$, Ca$^{2+}$ forms stronger complexes with NOM carboxylate groups, whereas the association of Na$^+$ with NOM is even weaker than

### Table 2

Diffusion coefficients of metal ions near the TNB molecule and in the aqueous phase

<table>
<thead>
<tr>
<th></th>
<th>NOM-associated</th>
<th>Bulk solution</th>
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<tbody>
<tr>
<td>$D$ (Na$^+$, $\times 10^{-5}$ cm$^2$/s)</td>
<td>1.42</td>
<td>1.42</td>
</tr>
<tr>
<td>$D$ (Ca$^{2+}$, $\times 10^{-5}$ cm$^2$/s)</td>
<td>~0 (bound to carboxyl)</td>
<td>0.67</td>
</tr>
<tr>
<td>$D$ (Mg$^{2+}$, $\times 10^{-5}$ cm$^2$/s)</td>
<td>0.12</td>
<td>0.89</td>
</tr>
</tbody>
</table>
the outer-sphere metal-NOM complexation observed for Cs⁺ [67,68]. The ionic behavior we observed in our simulations is in good qualitative agreement with these trends.

Our results are consistent with an alternative to our original hypothesis: divalent ions cause membrane fouling by enhancing the aggregation of NOM molecules in solution rather than by binding the carboxylate groups of the NOM directly to the sulfonyle groups of the PES membrane. Although truly dissolved NOM is not important in the fouling process, it can contribute to fouling after being aggregated by divalent ions. Some earlier studies suggested that higher membrane fouling in the presence of metal ions was due to the NOM aggregation [38,91], while others claimed that the presence of calcium simply neutralized the negative charge of the membrane surface [18]. The partially neutralized Cu²⁺-NOM complex may be more easily adsorbed at the membrane surface than a negatively charged NOM molecule. Thus, it is still probable that divalent ions associated with the NOM carboxylate groups may facilitate the adsorption of NOM at the membrane surface by partially neutralizing the negative charge of the NOM molecules. Within this line of reasoning, however, it still remains unclear whether fouling is caused by the cation-mediated NOM aggregation in solution or by stronger NOM–surface interactions in the presence of divalent ions. Since only one NOM molecule was used in the present model, NOM aggregation could not be studied in this work. More extensive MD simulations using multiple NOM molecules, employing much larger size of the simulated systems, and much longer simulation times (at least on the order of tens of nanoseconds) are currently in progress to quantitatively address the questions of NOM aggregation. The results of these large-scale MD simulations will be reported as they become available.

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