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Performance of a Hybrid ED-NF Membrane System for NOM Removal and Fouling Control

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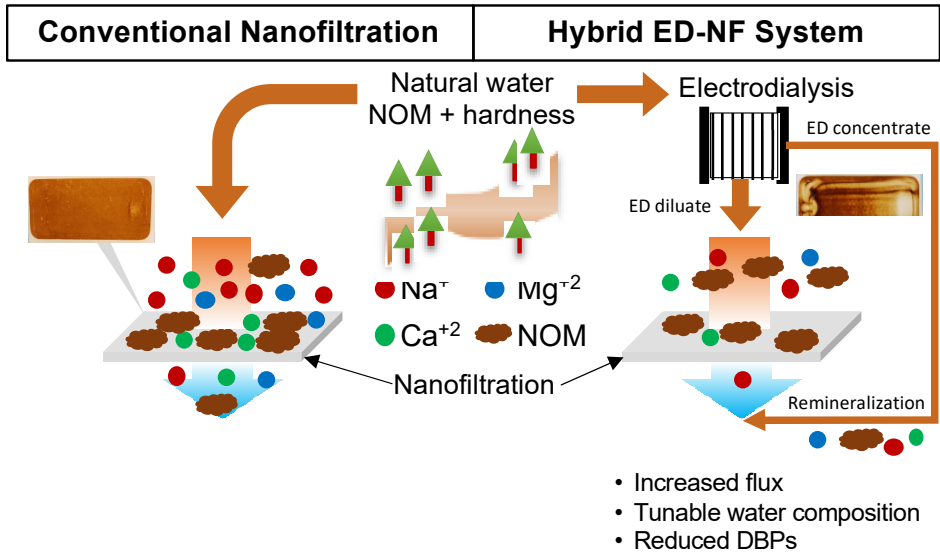
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1 **Abstract**

2 Natural organic matter (NOM) complicates water treatment and causes formation of
3 disinfection byproducts (DBPs). NOM is removed well by nanofiltration (NF) but causes
4 extensive membrane fouling, especially in the presence of divalent cations. This research
5 investigated a hybrid electro dialysis-nanofiltration (ED-NF) system to treat freshwaters
6 containing hardness and NOM. ED removes most ions but little to no NOM, and the ED diluate
7 is then treated with NF to remove NOM with reduced fouling. Subsequently, some or all of the
8 ED concentrate can be mixed with the NF permeate to increase water recovery, limit NOM
9 concentration (and thereby reduce DBPs), and control the ion content. Compared to NF alone,
10 ED-NF increases product water yield. NF fouling was reduced by the removal of divalent cations
11 in ED. Spectroscopic and resonant scattering measurements of fouled membranes near the
12 calcium K-edge reveal a significant contribution to NF fouling by calcium bridging between
13 carboxyl groups in NOM and on the membrane surface. This novel ED-NF system allows
14 several control “knobs” to increase water recovery and reduce DBP formation potential by
15 adjusting ED water recovery, ED diluate (and concentrate) ionic composition, and the fraction of
16 concentrate re-mixed with NF permeate to form the product water.

17 **Keywords:** Water treatment; Disinfection byproducts; Fouling mechanisms; X-ray spectroscopy;
18 Resonant X-ray scattering

19 Graphical Abstract



20

21

22 **1 Introduction**

23 Natural organic matter (NOM) is present in virtually all surface waters and includes
24 humic and non-humic fractions with a wide range of molecular weights and reactivities based on
25 sources and the presence of specific functional groups.^{1,2} NOM represents a major challenge in
26 water treatment; not only does it cause color and taste problems directly, but it reacts with
27 chlorine, the most commonly used disinfectant, to form potentially carcinogenic disinfection
28 byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs).^{3,4} The
29 reduction of DBPs in drinking water can be achieved by substituting other disinfection methods
30 for chlorination, removing DBPs precursors (e.g., NOM), and/or eliminating DBPs after
31 formation.^{5,6} These strategies to reduce DBPs in drinking water are reviewed briefly below, but
32 this research focused on systems that use nanofiltration (NF) for removal of the DBP precursor,
33 NOM. More specifically, since NOM often limits the productivity of NF membranes by fouling,
34 the objective of the research was to increase the water recovery in NF systems for drinking
35 water.

36 Water treatment processes for NOM removal include enhanced coagulation, advanced
37 oxidation, adsorption, and membrane technologies.^{5,7} Enhanced coagulation is a regulatory
38 requirement for conventional water treatment plants in the United States, but the targeted
39 dissolved organic carbon (DOC) removals (which depend on the influent alkalinity and DOC)
40 are relatively low and the process drastically increases production of residuals that need to be
41 managed.^{8,9,10} Advanced oxidation processes (AOPs) can achieve between 40-90% NOM
42 removal efficiency,¹¹ but the efficiency depends on the type and amount of organic matter and
43 the process creates smaller organics that are often biodegradable. Thus, AOPs are usually
44 coupled with other technologies such as membrane filtration, adsorption, and biodegradation.¹²

45 In the United States, adsorption has been used more commonly to target undesirable synthetic
46 organic chemicals (SOCs) such as pesticides and herbicides rather than NOM removal; NOM
47 removal by adsorption can vary widely over time and can reduce the efficiency for target SOC
48 either through competition for sites or pore-blocking by NOM.¹³ Ultrafiltration (UF) membranes
49 can effectively remove NOM with relatively high molecular weights but the pore sizes
50 (typically 30 to 1000 Å) allow most of the humic substances to pass through.

51 Nanofiltration (NF) can be an excellent solution for the removal of DBPs precursors
52 including the lower molecular weight fraction.⁵ NOM removal efficiencies achieved by NF can
53 exceed 80% and NF can be applied to various types of water.¹⁴⁻¹⁷ However, membrane fouling
54 decreases permeate flux and limits the utility of NF for NOM removal because of the loss of
55 productivity and added capital and operational costs;^{18,19} productivity here includes both
56 permeate flux and volume throughput (or water recovery) between chemical cleanings. NF
57 membrane fouling increases in the presence of cations, as NOM molecules and membrane
58 surfaces are often negatively charged due to specific functional groups (e.g., carboxylic acids)
59 and reduced electrostatic repulsion of the negatively charged macromolecules can lead to the
60 formation of dense/compact NOM fouling layers.^{15,20-22} Additionally, divalent cations such as
61 Ca^{2+} and Mg^{2+} can bridge negatively charged functional groups to significantly increase
62 fouling.^{15,21,23} Therefore, a pretreatment process to remove inorganic ions, particularly cations,
63 could considerably reduce NF membrane fouling and increase productivity during water
64 treatment. Precipitative softening to remove divalent cations prior to NF requires chemicals, such
65 as lime, and space for both coagulation/flocculation and sedimentation processes. Ion exchange
66 is simpler than lime softening, but increases Na^+ concentration in the finished water and
67 produces high salinity regeneration waste streams.^{24,25} Since NF membranes are currently used

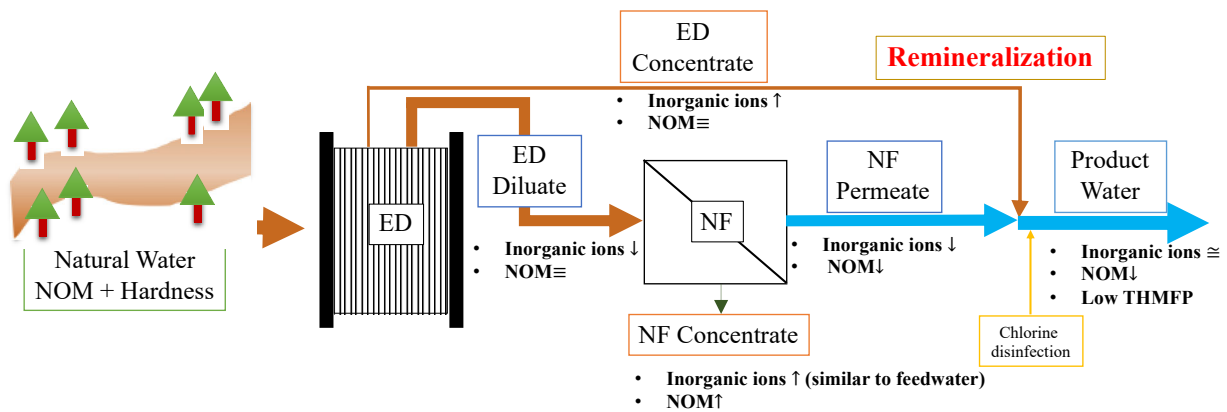
68 not only for NOM removal but also water softening (i.e., removal of multivalent cations),^{7,26,27}
69 softening pretreatment via NF holds some attraction because membrane systems are modular,
70 scalable, energy efficient, and minimize chemical use,^{28,29} but fouling, as indicated above, is
71 problematic.

72 Another possible (and heretofore unexplored) pretreatment strategy for NOM removal by
73 NF is electrodialysis (ED). ED is a technically verified water treatment technology with more
74 than a half-century of field-scale success at producing high quality water from brackish
75 water.^{30,31} ED separates charged molecules from feed waters using ion exchange membranes
76 (IEMs) but does not provide appreciable separation of NOM.³² Although acidic fractions of
77 NOM are negatively charged, NOM molecules exhibit low diffusivity due to their large size³³
78 and cannot pass through the low molecular weight cut-off IEMs used in ED.³⁴ A coupled RO/ED
79 system has been used to isolate/extract NOM from freshwater and seawater^{35,36}, but the studies
80 focused on NOM harvesting rather than drinkable water production and RO membrane fouling
81 mitigation. ED has been studied as a pretreatment to remove divalent cations in the presence of
82 NOM or neutral solutes, and [the researchers of those studies also found](#) that ED has a potential to
83 separate divalent ions without separation of NOM or neutral solutes.^{32,37} However, a complete
84 hybrid ED-NF process for NOM removal and NF fouling mitigation to improve productivity has
85 not been thoroughly investigated previously to our knowledge.

86 This research focuses on the development of a hybrid ED-NF membrane system to
87 remove NOM and increase the productivity of NF systems while providing appropriate ion
88 concentrations (for drinking water) in the final product water (Figure 1). With the proper choice
89 of the ion-exchange membranes, ED can remove most inorganic ions while achieving minimal
90 removal of NOM; subsequently, the ED diluate, containing few inorganic ions but NOM at

91 nearly the original concentration, can be treated by NF to remove NOM. In NF membrane
 92 systems for drinking water production, remineralization after NF treatment is often required
 93 because high removal of monovalent and/or divalent ions can produce unsavory and corrosive
 94 water.^{38,39} In this hybrid ED-NF system, some or all of the small volume of ED concentrate and
 95 the large volume of NF permeate can be combined to yield water with dramatically lower NOM
 96 concentration and ion concentrations appropriate for drinking water.

97 The total water recovery includes (some or all of) the ED concentrate and the NF
 98 permeate, so varying the ratio of ED concentrate to NF permeate mixed in the final step can be
 99 used to impact the recovery and tailor the resulting NOM and inorganic ion concentrations to
 100 desired values. With low resulting NOM concentration, disinfection of the resulting water by
 101 chlorination would result in acceptably low DBP concentrations.



102
 103 Figure 1. The proposed hybrid electro dialysis-nanofiltration (ED-NF) system for drinking water
 104 treatment of freshwaters containing natural organic matter (NOM) and hardness.

105 In a previous study for the ED part of this hybrid process, we found that NOM can be
 106 sorbed onto the IEM surface but ED can effectively separate alkaline earth metal ions without
 107 separation of NOM and without significant NOM sorption with proper IEMs.³² Here, we focus
 108 on the combination of ED and NF. To achieve the overall objective, tasks in this research were to

109 determine whether ED pretreatment is effective in reducing NF membrane fouling, to use
110 spectroscopic techniques to ascertain the causes of fouling, and to assess the DBP formation
111 potential of the hybrid ED-NF system product water. Fouling of the IEMs at the ED stage of the
112 hybrid ED-NF system was not investigated in this study, as it was considered in the previous
113 work.³² Technical evaluation metrics of the hybrid ED-NF system include the fractional water
114 yield, product water quality, and fouling characteristics of the NF membrane in the absence and
115 presence of ED pretreatment. The performance of the hybrid ED-NF system was evaluated for
116 three synthetic feedwaters containing NOM and one natural feedwater. DBP formation potential,
117 particularly trihalomethane formation potential, of the product water was evaluated using two
118 natural feedwaters to real treatment plants and compared to the formation potential of product
119 waters from the NOM removal processes currently employed at those plants. The fractional
120 recovery of the natural waters treated with the hybrid system to achieve a trihalomethane
121 formation potential (THMFP) below the US standard for THMs was estimated.

122 **2 Materials and methods**

123 **2.1 Experimental solutions**

124 Table 1 shows feedwater compositions for the experiments performed in this research; additional
125 details are in Sections 1 and 2 of the Supporting Information. This research employed five
126 different NOM sources: Lake Austin NOM (LAN), Suwannee River NOM (SNOM), Leonardite
127 Humic Acid (LHA), Texas Water NOM (TWN), and Florida Water NOM (FWN). SNOM and
128 LHA were purchased from the International Humic Substances Society (IHSS, St. Paul, MN).
129 LAN was extracted from Lake Austin in Austin, TX. Three synthetic feedwaters were prepared
130 using filtered (1.5 μm) stock solutions of LHA, SNOM, and LAN. NOM stock solutions were
131 diluted to 5 mg/L dissolved organic carbon (DOC) using Milli-Q water (Millipore, Bedford, MA,

132 USA) and the target amounts of ACS grade NaCl, CaCl₂·2H₂O (both from Fisher, Pittsburgh,
133 PA), and MgCl₂·4H₂O (AMResco, Solon, OH) were added to each synthetic feedwater. Since
134 membrane fouling is known to be exacerbated by divalent cations, all synthetic feedwaters
135 utilized the same background anion, chloride. Although we focus on cations in this study, ED
136 pretreatment can also combat membrane fouling/scaling caused by anions (carbonate, sulfate,
137 phosphate).

138 Florida Water (FWN) and Texas Water (TWN) were filtered (1.5 μm) and used with their
139 natural concentrations of all ions and NOM. FWN contains approximately 16.5 mg/L DOC, and
140 TWN contains approximately 4.5 mg/L DOC (Table 1). SNOM, LHA, LAN, and FWN were
141 used for the hybrid ED-NF system technical performance evaluation, and FWN and TWN were
142 used for DBP formation potential experiments.

143 Table 1. Feedwater compositions for hybrid ED-NF system technical performance evaluation and disinfection by-product potential
 144 experiments.

Type of feed	Feed Water ^a	Type of NOM	SUVA ₂₅₄ ^b (L/mg·m)	Conductivity (μ S/cm)	Ca mg/L	Mg (mg/L)	Na mg/L	DOC mg/L	Ca/DOC (mM/mM)	Note ^c
Synthetic freshwater	LAN	Lake Austin NOM	2.17±0.11 ^d	1224±2	68.2±0.4	7.3±0.8	112±10	5.1±0.4	4.02±0.20	I
	LAN W/ ED	(LAN)	2.13±0.17	245±0.4	7.3±0.1	0.7±0.1	25.1±1.6	5.2±0.3	0.42±0.02	
	SNOM	Suwannee River NOM	3.77±0.19	937±1	28.0±0.6	7.2±0.6	154±7	5.0±0.4	1.69±0.11	I
	SNOM W/ ED	(SNOM)	3.71±0.15	187±0.2	2.8±1.4	1.2±0.1	26.3±1.3	5.0±0.2	0.16±0.01	
	LHA	Leonardite Humic Acid	9.09±0.36	945±2	28.1±1.1	7.2±0.5	154±8	5.1±0.4	1.66±0.07	I
	LHA W/ ED	(LHA)	9.05±0.41	189±0.4	2.7±0.3	1.4±0.1	20.6±9.6	5.0±0.3	0.16±0.10	
Natural freshwater	FWN	Florida Water NOM (FWN)	3.74±0.05	720±9	84.4±0.6	13.3±0.5	36.8±2.7	16.5±0.5	1.54±0.04	I, II
	FWN W/ ED		3.64±0.38	144±4	7.3±1.6	1.6±1.2	9.7±0.6	16.7±0.5	0.13±0.03	
	TWN	Texas Water NOM (TWN)	2.89±0.08	449±7	61.0±2.7	10.5±1.1	22.1±6.8	4.5±0.1	4.07±0.10	II
	TWN W/ ED		2.85±0.18	90±1	7.6±1.5	1.8±0.3	8.7±0.5	4.5±0.1	0.51±0.10	

a. W/ED feeds are the ED pretreatment product waters (ED diluate) that were subjected to NF treatment; feeds without that designation were the influent to NF in the NF alone experiments and the influent to ED in the hybrid ED-NF system

b. Specific Ultra Violet Absorbance (SUVA₂₅₄) (L/mg·m) is an indicator of the relative fraction of aromatic NOM components and the hydrophobicity of NOM; a SUVA value greater than 4 suggests that the NOM contains high molar mass compounds and exhibits high hydrophobicity, whereas SUVA less than 2 suggests lower molar mass compounds and low hydrophobicity¹⁷.

c. Note specifies the experiments in which each feedwater was used: (I) technical performance evaluation tests; (II) DBP formation potential tests

d. \pm indicates 95% confidence intervals

145

146 **2.2 Bench-scale Electrodialysis and Nanofiltration experiments**

147 ED experiments were conducted using a batch-recycle ED experimental apparatus
148 (Figure S2), as described in our previous study.³² This apparatus consists of an electro dialyzer
149 and three streams: diluate (D), concentrate (C), and electrode rinse (E). ED pretreatment used 8 L
150 of diluate and 2 L of concentrate (i.e., 80% water recovery) with an 80% conductivity removal
151 goal. Details of the system are explained in Section 4 of the Supporting Information and are
152 essentially identical to those reported by Kum et al.³² The details of the specific energy
153 calculation (SEC) of the ED process are in Section 5 of the Supporting Information. In our
154 previous work we evaluated several different AEM/CEM pairs to identify a set that yielded the
155 lowest NOM adsorption; CMX/AMX IEM pair (Tokuyama Soda Co. Ltd. Japan) was chosen in
156 this study based on its good separation of inorganic ions with minimal organic matter
157 separation/sorption.^{32,40}

158 NF experiments were conducted using a laboratory-scale crossflow membrane system
159 (Figure S3); details of the system and its operation are in Section 6 of the Supporting
160 Information. The NF270 membrane (DuPont FilmTec™, Edina, MN) was chosen based on its
161 high permeate flux and NOM removal reported in previous research.⁴¹ All NF experiments were
162 performed at a constant applied pressure of 4.8 bar (70 psig), the pressure that was applied by the
163 manufacturer to identify the typical properties of NF270 membranes.⁴² Performance of the
164 hybrid ED-NF system was compared to the NF system without any pretreatment.

165 **2.3 Water Sampling and Qualitative Analyses of Samples**

166 Liquid samples were collected from the diluate/permeate and concentrate/feed of the
167 ED/NF systems during experiments. In ED experiments, 10 mL samples were pipetted from each
168 reservoir after each 10% reduction in conductivity from 10% to 80% to measure concentrations

169 of major cations (sodium, calcium, and magnesium) and the ultraviolet (UV) absorbance (254
170 nm), and 40 mL samples were withdrawn at the beginning and end to measure DOC
171 concentrations. In NF experiments, 50 mL of feedwater were withdrawn by pipette from the feed
172 reservoir and 50 mL of permeate were taken directly from the permeate stream at the beginning
173 of each experiment and every 24 hours for the duration of the NF experiments. Concentrations of
174 major cations and DOC, and the UV absorbance (254 nm), were measured for NF experimental
175 samples. NF experiments were run for six days with SNOM, LAN, and FWN, but the LHA
176 waters were run for only 24 hours due to higher fouling by this hydrophobic NOM.

177 Because cations significantly impact NOM fouling on membrane surfaces, our attention
178 was on cation removal rather than anion removal, as noted earlier. Concentrations of major
179 cations were measured via inductively coupled plasma-optical emission spectroscopy (ICP-OES,
180 Varian 710-ES, Varian, Inc, Palo Alto, CA). DOC concentrations were analyzed using a total
181 organic carbon analyzer (TOC-L CPH/CPN, Shimadzu, Japan). The ultraviolet absorbance at a
182 wavelength of 254 nm was measured using a diode array UV-Vis system (Agilent 8453, Agilent
183 Technologies, Santa Clara, CA) with a 1 cm path length quartz cell; specific ultraviolet
184 absorbance (SUVA₂₅₄) values were calculated as the ratio of UV absorbance and DOC.

185 **2.4 Membrane Surface Analysis**

186 Fouled and virgin NF membranes were dried and stored in a desiccator at atmospheric
187 pressure. Sections of each NF membrane were cut for *ex situ* investigation via scanning electron
188 microscopy (SEM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-
189 FTIR), and X-ray photoelectron spectroscopy (XPS). SEM (FEI Quanta FEG 650, Thermo
190 Fisher Scientific, Waltham, MA) was employed to identify foulants on the surface of the NF
191 membranes. Membrane samples were platinum-coated by a benchtop sputter coater (Cressington

192 208, Cressington Scientific Instruments, UK) before SEM analysis. ATR-FTIR measurements
193 provided detailed information on the functional groups present in the membranes and fouling
194 layers with a sampling depth of approximately 0.7 μm ,⁴³ while surface-sensitive XPS provided
195 chemical information for the top-most portion of the fouling layer (i.e., sampling depth less than
196 10 nm).⁴⁴ Detailed information on ATR-FTIR and XPS measurements is in Sections 11 and 12 of
197 the Supporting Information, respectively.

198 Furthermore, *ex situ* membrane samples were analyzed using near edge X-ray absorption
199 fine structure (NEXAFS) spectroscopy and tender resonant X-ray scattering (TReXS) near the
200 calcium K-edge on beamline 12-ID-C at the National Synchrotron Light Source II (Brookhaven,
201 NY, USA); as explained subsequently, similar measurements for magnesium would require a
202 different beamline and separate preparation and were not performed. NEXAFS spectroscopy is
203 sensitive to specific chemical bonds and functional groups, so investigation near the Ca K-edge
204 provides insight into the chemical environment of calcium in the fouling layers.⁴⁵ Meanwhile, X-
205 ray scattering probes spatial periodicities to distinguish the structural arrangements and material
206 morphology. By tuning the X-ray energy near the absorption edge of core-level electronic
207 transitions in calcium atoms using tender X-rays, TReXS can provide added contrast to help
208 probe the distribution of calcium in the membrane samples.⁴⁶ Samples were prepared by
209 carefully removing the fabric backing of the membranes and mounting the resulting thin films
210 comprised of a fouling layer, a polyamide/piperazine active layer, and a polysulfone support
211 layer (~50-60 μm total thickness, Table S4) on 10 mm washers. Fluorescence-yield NEXAFS
212 spectra and transmission TReXS data were collected at energies near the calcium K-edge (4030-
213 4075 eV) using a Pilatus 300KW detector (Dectris, Philadelphia, PA, USA). Attenuation lengths
214 of tender X-rays through representative membrane/foulant materials (Table S6) are between 20

215 and 50 μm on-resonance and between 95 and 120 μm off-resonance,⁴⁷ indicating that the fouling
216 layers (<10 μm thick, Table S4) were fully probed during NEXAFS and TReXS measurements.
217 Additional information on these measurements is in Section 13 of the Supporting Information.

218 **2.5 Disinfection by-products formation potential experiments**

219 Trihalomethane formation potential (THMFP) experiments were conducted using the two
220 natural feedwaters (TWN and FWN) to evaluate the water recovery possible when the ED-NF
221 system is used to limit DBPs in the final product water. The THMFP of product waters from the
222 hybrid ED-NF system was compared to that obtained by the existing NOM removal processes
223 employed at the treatment plants. The plant with TWN as its source water uses enhanced
224 coagulation to reduce NOM concentrations; poly-aluminum chloride coagulant was acquired
225 from the plant and used for this research. The plant with FWN as its source water applies NF to
226 reduce hardness and NOM concentration, so we compared the hybrid ED-NF treated water to
227 water treated by NF alone. Since FWN has a very high NOM concentration, only 50% of the ED
228 concentrate was mixed with the NF permeate in the hybrid ED-NF system. THMFP tests were
229 conducted based on Standard Method 5710B⁴⁸ and THM analyses were performed following US
230 Environmental Protection Agency (US EPA) Method 551.1.⁴⁹ Briefly, samples were spiked with
231 free chlorine (to yield residuals of 2 - 5 mg/L at day 7) and reacted for 7 days in the dark at 25
232 $^{\circ}\text{C}$, followed by extraction of THMs into pentane and determination of THM concentrations via
233 gas chromatography with an electron capture detector.

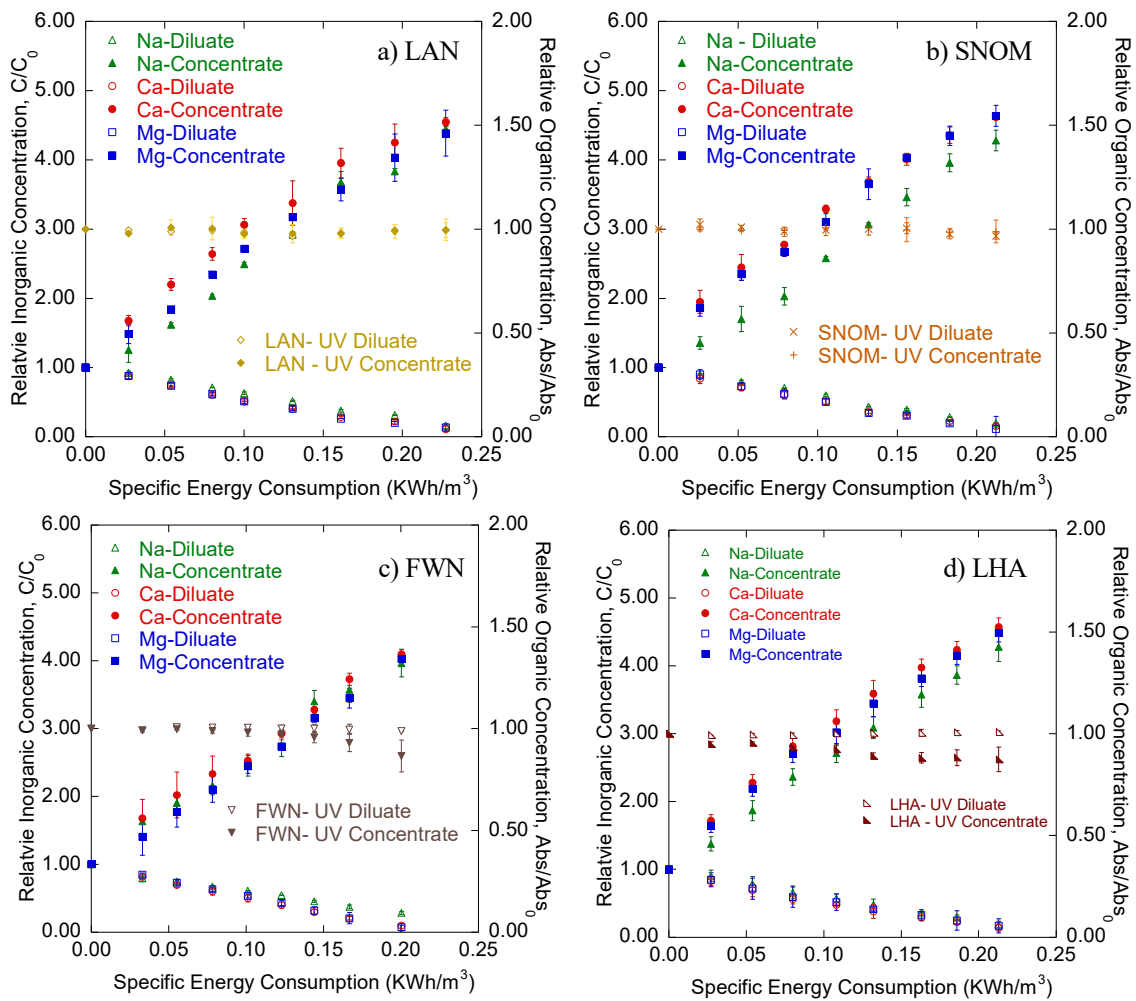
234 3 Results and Discussion

235 3.1 ED pretreatment provides selective removal of cations

236 Using four NOM sources, the ED pretreatment performance as a function of NOM source
237 characteristics could be examined (Figure 2). In Figure 2, the abscissa is the specific energy
238 consumption (SEC, a normalized measure of the energy use to accomplish given amounts of
239 separation), the left ordinate is the normalized concentration of Na^+ , Ca^{2+} , and Mg^{2+} , and the
240 right ordinate is the normalized UV absorbance (taken as a measure of NOM content). In ED
241 experiments with all four NOM sources, the CMX membrane provided greater relative
242 separation of Ca^{2+} and Mg^{2+} compared to Na^+ , at least in the early stages of the experiments. This
243 cation separation trend is more obvious in the concentrate stream, which could reach at most five
244 times the initial feed concentration of cations (the volumes of concentrate and diluate are 2 L and
245 8 L, respectively). This result is consistent with previous studies^{32,50,51} and is attributed to the
246 selectivity of sulfonic acid groups in the CMX membrane for multivalent cations over
247 monovalent cations.⁵² (Note, however, that for all but FWN, the molar concentration of Na^+ --and
248 therefore the molar flux through the CEM--was substantially higher than that of the divalent
249 cations.)

250 For both LAN (Figure 2a) and SNOM (Figure 2b), the relative UV absorbance ratio in
251 the diluate and concentrate streams stayed near one throughout the entire ED experiment, and
252 DOC concentrations and SUVA_{254} values in the diluate before and after ED pretreatment were
253 similar (Table 1). Each of these trends indicates that little NOM separation and little NOM
254 sorption to the IEMs occurred; total NOM mass loss during ED pretreatment was less than 1%
255 for both LAN and SNOM. Generally, if a NOM contains a large number of hydrophobic
256 components, the NOM likely has a SUVA_{254} value over 4 and contains substantial fraction of

257 NOM with molecular weights over 10000 Da.^{16,17,53} According to the SUVA₂₅₄ values (Table 1)
 258 and NOM molecular weight distributions (Figure S4), both NOMs have the SUVA₂₅₄ value less
 259 than 4, and the weight-averaged molecular weights (Table S3) of LAN and SNOM are 750 Da
 260 and 1260 Da, respectively, indicating LAN and SNOM are less likely to contain hydrophobic
 261 components; the results were consistent with this expectation in that the LAN and SNOM
 262 sorption to the IEMs during ED pretreatment was minimal.



263
 264 Figure 2. Electrodialysis pretreatment separates inorganic ions (Ca²⁺, Mg²⁺, Na⁺) but does not
 265 provide significant NOM separation at 80% water recovery and 80% conductivity separation.
 266 Error bars represent 95% confidence intervals.

267 Since the initial conductivity of FWN is the lowest among the four NOM solutions (Table
268 1), the total SEC of ED to achieve the separation goal for FWN was less than that of the others.
269 In FWN, the calcium removal was greater than sodium in the diluate stream, but the degree of
270 calcium separation in the concentrate stream at the end of the experiment was not as significant
271 as observed in LAN and SNOM experiments; these observations could be due to calcium
272 carbonate precipitation and/or the IEM fouling in the concentrate. FWN is a natural freshwater
273 containing alkalinity and a relatively high calcium concentration. As ED removes inorganic ions
274 in the diluate, both the calcium and carbonate concentration in the concentrate increases;
275 therefore, there is a chance for calcium carbonate precipitation since the pH of concentrate
276 stream is above 7.8 and the saturation index (the ratio of the ion activity product to the saturation
277 equilibrium constant) of calcite (CaCO_3) rises to 55 ($\log \text{SI} > 1$, oversaturated) at the end of the
278 ED experiment. In experiments with FWN, we again observed that the UV absorbance and DOC
279 concentrations in the diluate (Figure 2c and Table 1) before and after ED pretreatment did not
280 change significantly, but there was a nearly 14% UV absorbance and 5% DOC decrease in the
281 concentrate after ED pretreatment. These losses suggest that some NOM from the concentrate
282 stream sorbed to the IEMs during ED pretreatment, but minimal sorption occurred to the diluate
283 side of the membranes. The greater reduction in UV compared to DOC suggests that the more
284 hydrophobic fraction of NOM sorbed preferentially. This IEM fouling in the concentrate could
285 be due to the relatively high initial divalent ion concentration in the FWN solution; the calcium
286 and magnesium concentrations in the concentrate stream rose to nearly 8.5 mM and 2.2 mM,
287 respectively at 80% water recovery. In addition to high hardness concentrations, the high DOC
288 of FWN (16.5 mg/L) could have contributed to the observed NOM mass loss in the concentrate.

289 The inorganic ion separation trends with LHA are similar to those for the other waters,
290 but the organic separation trends show differences. Since LHA is a soil NOM and more
291 hydrophobic than the other NOM sources, it has greater tendency to sorb to the IEMs during ED,
292 and our results show LHA separation during ED not because of actual organic compound
293 separation through the IEMs but due to sorption to the IEMs in the concentrate.³² Meanwhile,
294 minimal changes in UV absorbances, DOC concentrations, and SUVA₂₅₄ values in the diluate
295 stream (Figure 2d and Table 1) indicate that IEM fouling only occurred in the concentrate
296 stream. At the end of ED pretreatment, the losses of UV and DOC were similar to those for
297 FWN; UV absorbance and DOC decreased by 17% and 7% in the concentrate, respectively.
298 Moreover, the amount of NOM sorption increased as the inorganic ion concentration increased in
299 the concentrate stream (Figure 3d). As the ionic strength rises with the percent of water recovery,
300 NOM molecules become coiled and compact,¹⁵ thereby increasing the likelihood of membrane
301 surface adsorption and bridging by the increased divalent cation concentrations in the
302 concentrate. Additionally, both the AEM and CEM can be fouled by NOM in the concentrate,
303 but AEMs tends to exhibit greater fouling by NOM than CEMs because AEMs attract negatively
304 charged NOM to the membrane surface;³² therefore, if the feed solution for ED pretreatment is
305 similar to FWN (high NOM and calcium concentrations) or LHA (high SUVA₂₅₄ values),
306 additional efforts such as controlling pH, adding antiscalants, or choosing AEMs with minimal
307 NOM interaction, might be required to prevent NOM adsorption to the IEMs from the
308 concentrate and allow ED pretreatment to realize its full potential.

309 **3.2 Improvements in NF permeate flux and water recovery following ED**
310 **pretreatment**

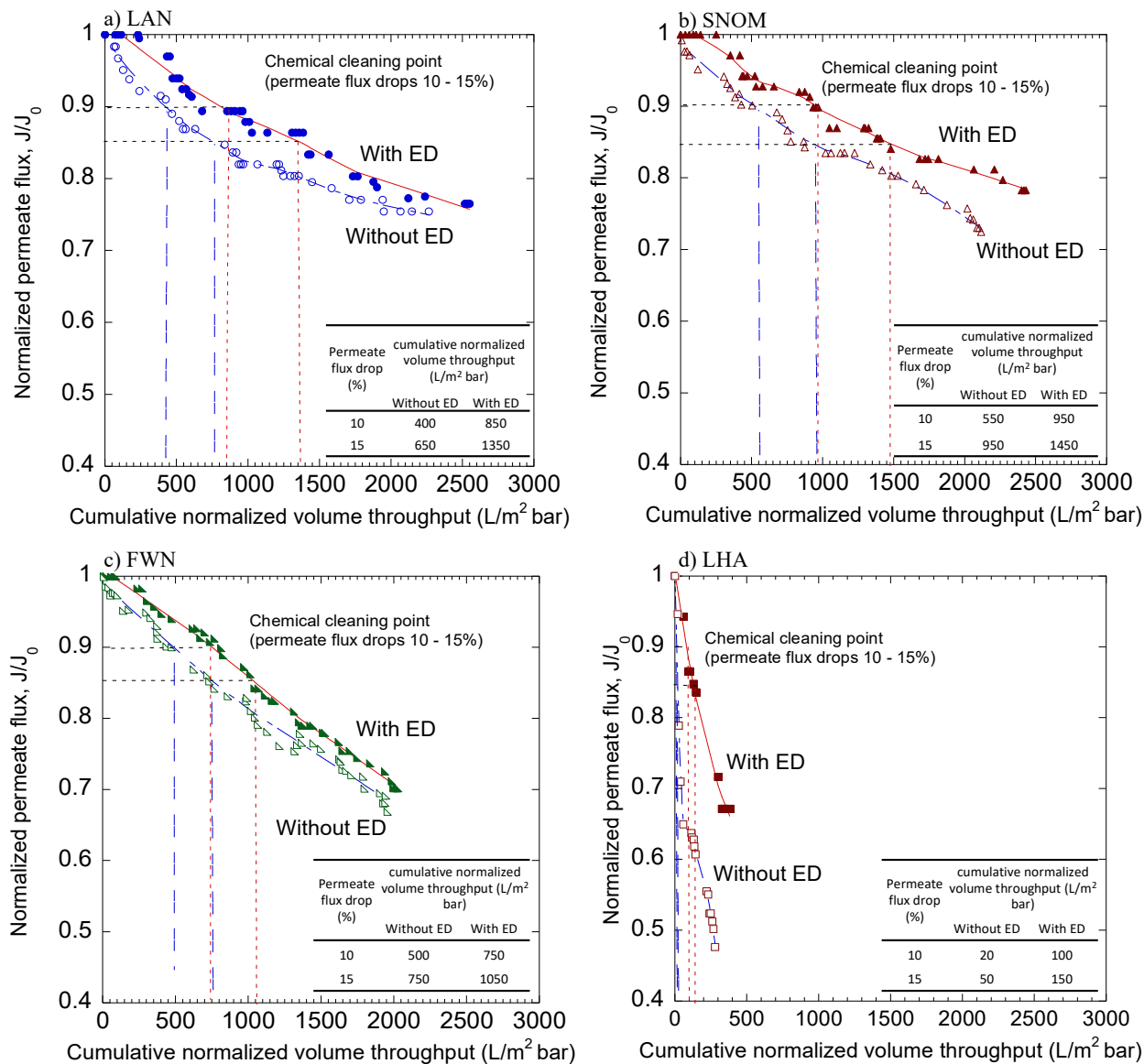
311 To evaluate the impact of ED pretreatment on NF performance, NF experiments without
312 and with ED pretreatment were operated for 144 hours with LAN, SNOM, and FWN and for 24
313 hours with LHA due to increased fouling by this hydrophobic NOM. The normalized permeate
314 flux decline as a function of the cumulative normalized volume throughput for the four NOM
315 sources without and with ED pretreatment is shown in Figure 3.

316 In all cases, the normalized permeate fluxes with ED pretreatment are higher than without
317 ED pretreatment immediately after the experiment begins; that is, ED pretreatment delays NOM
318 fouling on the membrane surface and improves the water production rate at constant applied
319 pressure due to the lower ion concentrations in the NF feed solution following ED (Table 1). The
320 permeate fluxes without ED pretreatment decreased immediately at the beginning of system
321 operation, an indication that the presence of divalent cations (Figure S6) and relatively high ionic
322 strength of the untreated water led to rapid NOM fouling of the NF membrane. Indeed, a set of
323 experiments with SNOM that isolated the effects of the three cations (Na^+ , Ca^{2+} , and Mg^{2+}) and
324 reported in Section 10 of the Supporting Information showed that the presence of calcium or
325 magnesium ions leads to approximately 20% more permeate flux decline and 7-8% less water
326 production after 144 hours relative to experiments with SNOM and sodium.

327 The results in Figure 3 indicate that the flux decline rate slowed at the end of NF
328 operation in SNOM and LAN, but FWN and LHA had continuous flux decline throughout the
329 experiments. The higher NOM concentration in FWN, the greater hydrophobicity of LHA, and
330 the high molecular weight fractions of these two NOM sources (Figure S4) are the likely causes
331 for this observed behavior. ED pretreatment improved the flux in all cases, but the impacts of the

332 composition and concentration of the NOMs on NF fouling persisted. In this work, the ED
333 system targeted only 80% removal of conductivity; however, optimization of ion removal during
334 ED could yield greater improvement of NF flux.

335 Pressure membranes are often cleaned when the normalized permeate flux declines by 10
336 to 15% from the initial stabilized flux.^{54,55} On Figure 3, the 10% and 15% permeate drop points
337 are marked on the trend lines and the associated cumulative normalized volume throughput
338 values are indicated. At the 10% flux decline, ED pretreatment improves the product water yield
339 by approximately 100% for LAN, 60% for SNOM and FWN, and 400% for LHA. ED
340 pretreatment increases the product water yield, extends the NF operating period, and thereby
341 reduces chemical use.



342

343 Figure 3. Normalized permeate flux decline as a function of cumulative normalized volume

344 throughput in the NOM feed solutions without and with ED pretreatment reveal an increase in

345 permeate flux and total volume throughput following ED pretreatment: a) Lake Austin NOM

346 (LAN), b) Suwannee River NOM (SNOM), c) Florida Water NOM (FWN), and Leonardite

347 Humic Acid (LHA). Smoothing lines are provided to highlight trends.

348 **3.3 Increased removal of NOM and cations by ED-NF relative to NF**

349 The NF270 membrane is relatively hydrophilic and negatively charged, and has a
350 molecular weight cut-off of 155 Da (Table S2);^{56,57} therefore, it impedes some substances from
351 passing through the membrane by electrostatic repulsion and rejects substances larger than 155
352 Da by size exclusion. Table 2 presents inorganic ions and organic (i.e., DOC) removal
353 efficiencies achieved by NF without and with ED pretreatment. The removal efficiency of
354 inorganic cations increased after ED pretreatment as a result of fewer inorganic ions in the NF
355 feed solution after ED pretreatment and an increase in the permeate flux in NF experiments
356 following ED pretreatment. Although the differences in NOM removal efficiency between NF
357 experiments without and with ED pretreatment are quite small, these differences were found to
358 be statistically significant ($P\text{-value} \leq 0.05$) for LAN, SNOM, and LHA. Moreover, as the NOM
359 fouling layer on the membrane surface continuously builds, the NOM removal efficiency
360 remained fairly consistent throughout NF experiments, suggesting that fouling has little impact
361 on NOM removal efficiency. Regardless, ED pretreatment improves the quality of the product
362 water due to the partial desalination of the NF feedwaters.

363 Table 2. Rejection of inorganic cations and NOM by the NF270 membrane without and with ED
 364 pretreatment. (Values in table represent % removal in NF treatment)

Type of NOM		LAN		SNOM		FWN		LHA		Control**
Pretreatment		None	ED	None	ED	None	ED	None	ED	None
Removal Efficiency* (%)	Ca	42±2	73±2	47±1	71±4	34±5	80±2	46±1	76±4	45±2
	Mg	62±1	70±1	74±2	77±3	45±3	80±3	51±2	74±1	76±2
	Na	22±1	43±1	32±0.3	48±2	18±4	56±3	32±1	56±4	19±2
	DOC	89.9 ±0.6	93.1 ±0.8	92.5 ±0.9	93.9 ±0.6	94.8 ±0.4	95.5 ±0.5	89.9 ±3.5	91.9 ±3.3	N/A

*± indicates 95% confidence intervals

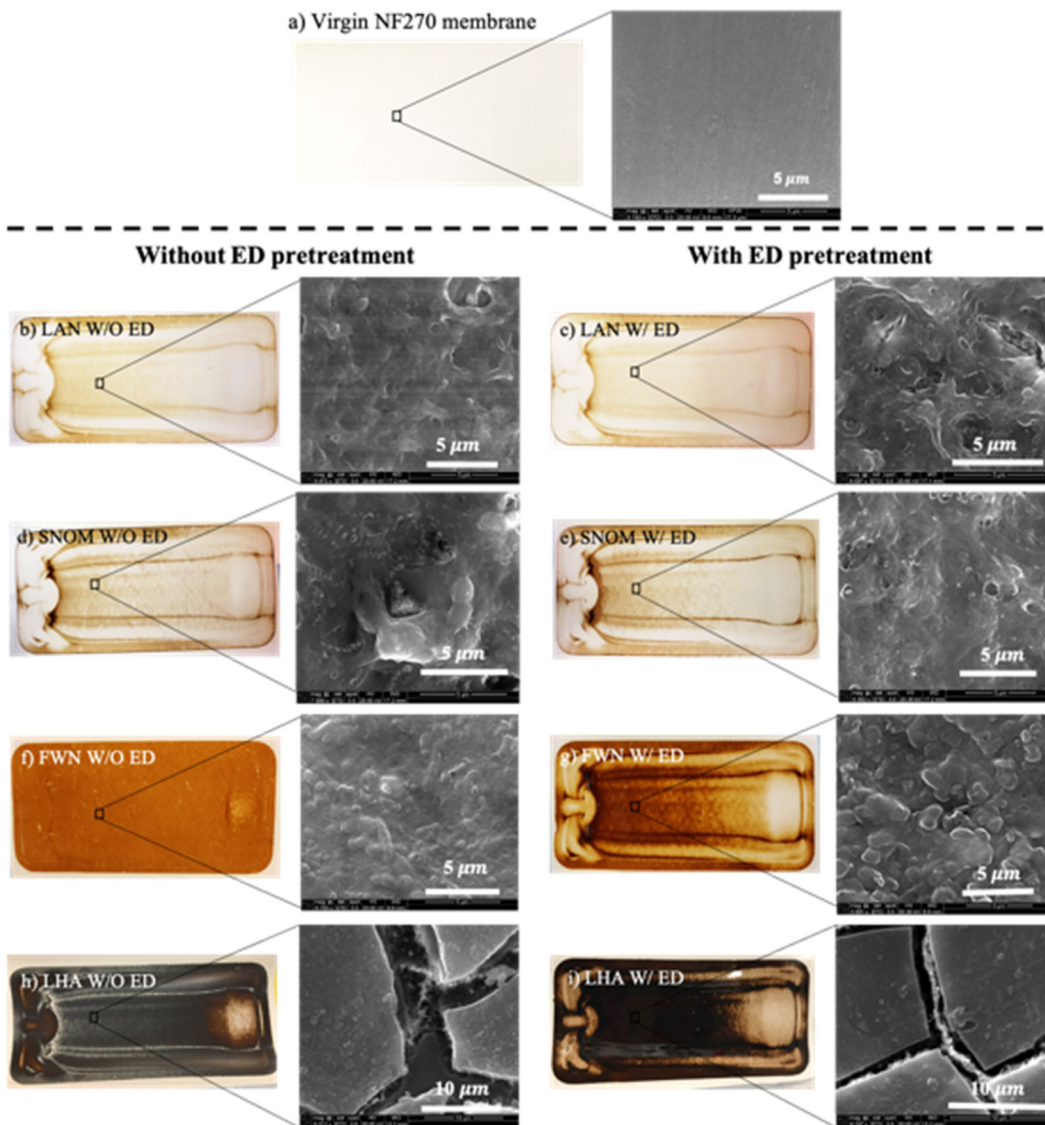
**Control experiment were carried out with the synthetic feed water for SNOM and LHA without NOM

365 3.4 Investigation of fouling-related benefits of the ED-NF system

366 3.4.1 Reduced visual fouling of NF membranes following ED pretreatment

367 Photographic and SEM images of NF membranes before and after fouling experiments
 368 are presented in Figure 4. Recall that the NF operation duration was 24 hours for LHA and 144
 369 hours for the other three NOMs. NOM fouling is evident for all four NOMs based on the color
 370 change from the original white virgin membrane (Figure 4a), and SEM images of fouled
 371 membranes confirm that the fouling of the membrane is mainly due to accumulation of NOM
 372 rather than mineral scaling (e.g., calcite). The degree of NOM fouling depends on the type and
 373 initial concentration of NOM, and the absence/presence of ED pretreatment. Optically, the
 374 degree of NOM fouling by LAN is the least among the four NOMs, but NOM aggregates are
 375 observed in SEM images (Figure 4, parts b and c). Both photographic and SEM images of
 376 SNOM fouled membranes (Figure 4, parts d and e) are similar to LAN except for the notably
 377 darker color due to the color of SNOM (Figure S1). Visible differences between the membrane
 378 surfaces without and with ED pretreatment for LAN and SNOM are observed with careful
 379 examination—more dark area in the membrane surface without ED pretreatment. Although flux

380 decline results for LAN and SNOM (Figure 3, parts a and b) highlight differences in fouling
381 between the experiments without and with ED pretreatment, visible differences between the
382 membrane surfaces without and with ED pretreatment for LAN and SNOM are less significant,
383 suggesting that fouling mechanisms are similar in these experiments (Figure 4, parts b to e).



384
385 Figure 4. Photographic and SEM images of the virgin NF270 membrane (top) and membranes
386 fouled by the four NOM sources without (left) and with (right) ED pretreatment show a visual
387 decrease in NOM fouling following ED pretreatment.

388 Visible differences in the NF membrane surfaces between the experiments without and
389 with ED pretreatment are observed for FWN and LHA. The high NOM concentration in FWN
390 promotes additional NOM accumulation on the membrane surface (Figure 4, parts f and g), and
391 these solutions had the second most dramatic flux declines (Figure 3). Additionally,
392 colloids/particles in FWN (observed via nanoparticle tracking analyses, Figure S5) may
393 contribute to fouling via deposition/cake layer formation. Although the operation time for LHA
394 was only 1/6 of that for the other NOMs, the images in Figure 4, parts h and i, clearly
395 demonstrate that LHA caused significant NOM fouling. In fact, cracking of the LHA foulants
396 occurred upon drying due to excessive accumulation of NOM on these membranes. These results
397 explain the dramatic permeate flux declines of LHA (Figure 3d). The higher fouling potential of
398 LHA can be explained by its higher average molecular weight (Figure S4) and its greater
399 hydrophobicity, as it is a soil NOM.⁵⁸ The NF270 membrane is a very hydrophilic membrane
400 (i.e., its water contact angle is 27°, Table S2), but it is semi-aromatic polyamide thin-film
401 composite membrane, containing some hydrophobic structure in it, as a result, hydrophobic
402 fractions of the NOM likely sorbed to the membrane. Although high NOM concentration (FWN)
403 and high NOM hydrophobicity (LHA) enhance NOM fouling during NF, both FWN and LHA
404 visibly show significant fouling mitigation after ED pretreatment.

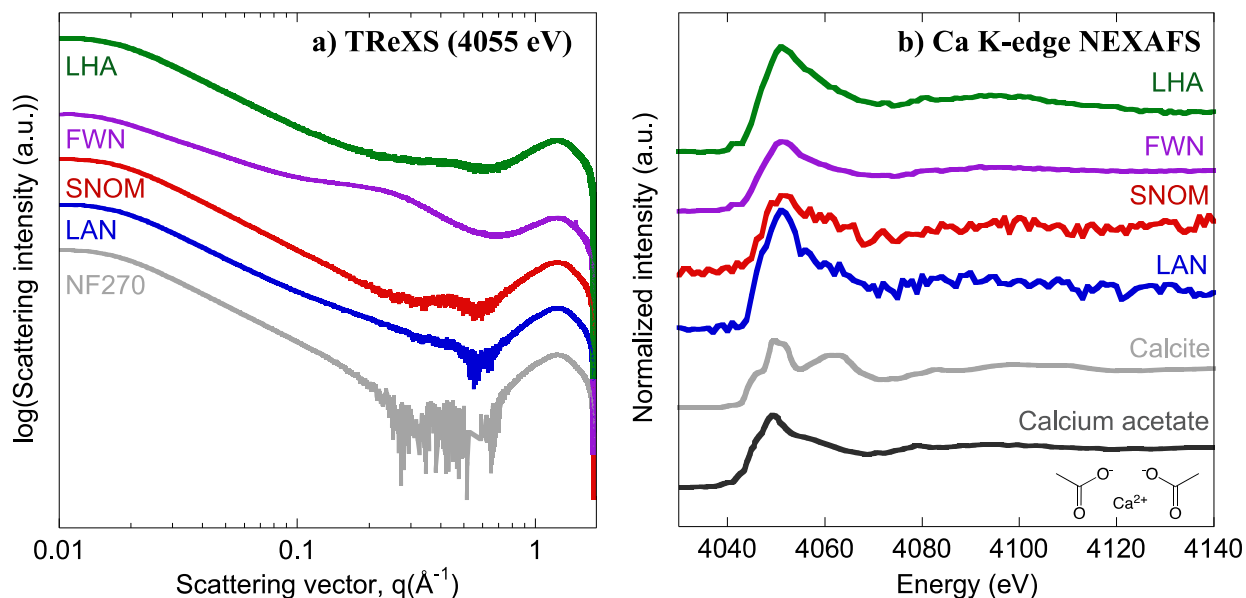
405 Another benefit of the ED pretreatment is the significant reduction in conductivity and
406 ionic strength that was evident in the NF feed waters (Table 1). Variation in ionic strength
407 influences NOM size/shape (e.g., coiling and aggregation), which likely impact the density and
408 compaction of the fouling layers. The lower ionic strengths associated with ED pretreatment may
409 have also contributed to reductions in flux and fouling.

410 3.4.2 Elucidation of fouling mechanisms using spectroscopy and scattering

411 To further unravel the important fouling mechanisms that influence the performance of
412 this hybrid ED-NF system, several conventional- and synchrotron-based characterization
413 techniques were employed. The goals of these analyses were to determine the contributions of
414 calcium to NF membrane fouling and to elucidate the mechanisms of NF membrane fouling in
415 the ED-NF system. While magnesium also contributes to NOM fouling of NF membranes
416 (Section 10 of the Supporting Information), calcium was chosen as the model inorganic species
417 for this investigation due to its presence in the feedwaters at higher concentrations than
418 magnesium (Table 1) and the absence of any magnesium signal during preliminary XPS survey
419 scans.

420 Figure 5 presents Ca K-edge TReXS (a) and NEXAFS (b) results of the NF membranes
421 fouled by waters without ED pretreatment; results were similar for the membranes fouled by ED
422 pretreated waters, as shown in Figure S11. TReXS results of the fouled membranes near the Ca
423 K-edge reveal broad scattering features in the q -range $0.2\text{-}0.5 \text{ \AA}^{-1}$ (**Error! Reference source not**
424 **found.a**) that are not present in the virgin NF270 membrane. The broad features in the q -range
425 $0.2\text{-}0.5 \text{ \AA}^{-1}$ are specific to the fouling layers and correspond to characteristic length scales,
426 $d=2\pi/q$, in the range $1.7\text{-}2.8 \text{ nm}$. Meanwhile, the feature near 1.2 \AA^{-1} present in all samples is
427 attributed to the so-called amorphous halo that is typically seen for amorphous polymers and it is
428 likely coming from the polysulfone support layer of the NF270 membrane.⁵⁹ Scattering at
429 energies near an elemental absorption edge enhances the contrast of the absorbed element due to
430 changes in the complex index of refraction such that the spatial distribution of the absorbed
431 element can be probed with greater sensitivity⁶⁰, as highlighted in previous research that
432 employed TReXS near the sulfur K-edge to determine the phase segregation of perfluorinated

433 sulfonic acid membranes.⁶¹ In this study, characteristic length scales obtained near the Ca K-
434 edge likely correspond to the average spacing between calcium atoms within the fouling layers.



435
436 Figure 5. (a) TReXS results of NF membranes fouled by the four NOM sources following ED
437 pretreatment and the virgin NF270 membrane near the Ca K-edge reveal distinct scattering
438 features in fouled membranes that represent the spacing of NOM-calcium-NOM and/or NOM-
439 calcium-membrane complexes within the fouling layers. (b) Calcium K-edge NEXAFS spectra
440 of membranes fouled by the four NOM sources with ED pretreatment suggest calcium bridging
441 of carboxylate groups as a fouling mechanism, per their agreement with the spectra of calcite and
442 calcium acetate (taken from Guo et al.⁶²). The results are similar regardless of ED pretreatment,
443 see Section 13 of the Supporting Information.

444 The characteristic length scales of calcium in the fouling layers obtained from Ca K-edge
445 TReXS (1.7-2.8 nm) are similar to the estimated NOM molecule sizes per size exclusion
446 chromatography results (1.2–2.6 nm, Table S3). Although the distribution of interacting
447 functional groups varies as a function of NOM source/composition, the general agreement

448 between length scales obtained from the two techniques suggests that interactions between
449 calcium and NOM contribute to fouling of the NF membranes. The FWN-fouled membranes
450 exhibit a more intense scattering peak centered at lower q compared to the other samples,
451 suggesting a greater number of scatterers (i.e., more calcium atoms) and a larger characteristic
452 length (i.e., more spacing between calcium atoms) in FWN fouling layers relative to other
453 samples. The increased amount of calcium in the FWN fouling layers may be due in part to the
454 higher NOM and calcium concentrations in the FWN feedwater, which led to increased
455 incorporation of calcium in FWN fouling layers relative to the other samples. The larger
456 characteristic length in FWN fouling layers is attributed to the high molecular weight fraction of
457 FWN observed in size exclusion chromatography (Figure S4), which likely consists of
458 macromolecules and/or polysaccharides with larger spacing of interacting functional groups
459 relative to low molecular weight NOM fractions.

460 The Ca K-edge TReXS results indicate contributions of interactions between calcium,
461 NOM, and membrane surfaces to NF fouling, so further spectroscopic investigation aimed to
462 determine the mechanisms by which fouling occurs during NF. Ca K-edge NEXAFS spectra of
463 the fouled membranes reveal a similar local chemical bonding environment around calcium
464 among the samples (i.e., all NOM sources, with and without ED pretreatment) that is consistent
465 with the spectrum of calcium acetate, a surrogate compound to represent calcium bridging of two
466 carboxylate groups (**Error! Reference source not found.**)^{63,64} The agreement in these spectra
467 to that of calcium acetate indicates that calcium bridging of carboxylate groups is the primary
468 mechanism by which calcium interacted with NOM and the membrane surface during NF
469 fouling experiments. ATR-FTIR spectra (Figure S7) and C 1s XPS spectra (Figure S8) of fouled
470 membranes confirm the presence of carboxyl groups in the fouling layers, in agreement with

471 previous studies on NOM fouling of NF membranes.¹⁹ SEM images (Figure 4) and Ca K-edge
472 NEXAFS (Figure 5b) show no signs of calcite scaling, ruling out this fouling mechanism in the
473 current study.

474 Surface-sensitive Ca 2p XPS results (Figure S9) suggest a decrease in the amount of
475 calcium in the top-most surface region of fouling layers formed during experiments with ED
476 pretreatment relative to experiments without ED pretreatment for all four NOM sources. The
477 XPS spectra predominantly captured NOM-Ca-NOM interactions due to the low penetration
478 depth (<10 nm) of XPS measurements. Meanwhile, Ca K-edge jump ratios based on NEXAFS
479 spectroscopy (Section 13 of the Supporting Information), which have been proposed by Osawa⁶⁵
480 to represent the relative amount of an element in a homogeneous material, are similar between
481 NF experiments without and with ED pretreatment; differences range from 1.0 percent for
482 SNOM to 6.8 percent for FWN. Given that the thickness of the fouling layers without and with
483 ED are similar for a given NOM (Table S4) and the NEXAFS measurements fully probed the
484 fouling layers, the similarity in the Ca K-edge jump ratios suggests that similar amounts of Ca
485 were present throughout the entire fouling layer thickness without and with ED pretreatment.
486 Perhaps, the increased depth penetration in NEXAFS compared to XPS captured both the NOM-
487 Ca-membrane interactions as well as the NOM-Ca-NOM interactions. Taken together with the
488 XPS data, which shows a decrease in Ca in the top surface of the fouling layer with ED
489 pretreatment, it is possible that a gradient in calcium concentration developed in the fouling layer
490 with ED pretreatment. The gradient of calcium in the fouling layers could be due to
491 concentration polarization, among other factors.

492 The conventional ATR-FTIR and XPS and synchrotron TReXS and NEXAFS results all suggest
493 the importance of Ca-bridging as a major NF fouling mechanism associated with all of the

494 NOMs regardless of pretreatment. However, additional contributions to fouling from other
495 mechanisms (e.g., hydrophobic interactions, mineral scaling) also influence the performance of a
496 hybrid ED-NF system. For instance, LHA-fouled membranes exhibit peaks characteristic of soil
497 NOM fractions such as aromatic C=C stretching (Figure S7), suggesting that hydrophobic
498 interactions between LHA and the membrane surface significantly contributed to fouling by this
499 NOM. In this study, the inclusion of the Ca-specific synchrotron data highlighted the ability to
500 identify Ca-carboxylate length scales within the fouling layers. The NEXAFS results allowed
501 identification of Ca-bridging to carboxylate groups at greater depth penetration than XPS,
502 thereby providing additional insight into interactions, including those at the membrane-fouling
503 layer interface. While synchrotron techniques have previously been employed to study calcium
504 bridging of organic matter and mineral surfaces,⁶⁶ this work is among the first to apply these
505 tools, especially resonant X-ray scattering, to describe membrane fouling, thus opening the door
506 for future work in this space.^{67,68} In particular, a complementary synchrotron investigation at the
507 Mg K-edge would be insightful regarding the specific interactions between divalent cations and
508 NOM that influence membrane fouling.

509 **4 Engineering Applications for the ED-NF system**

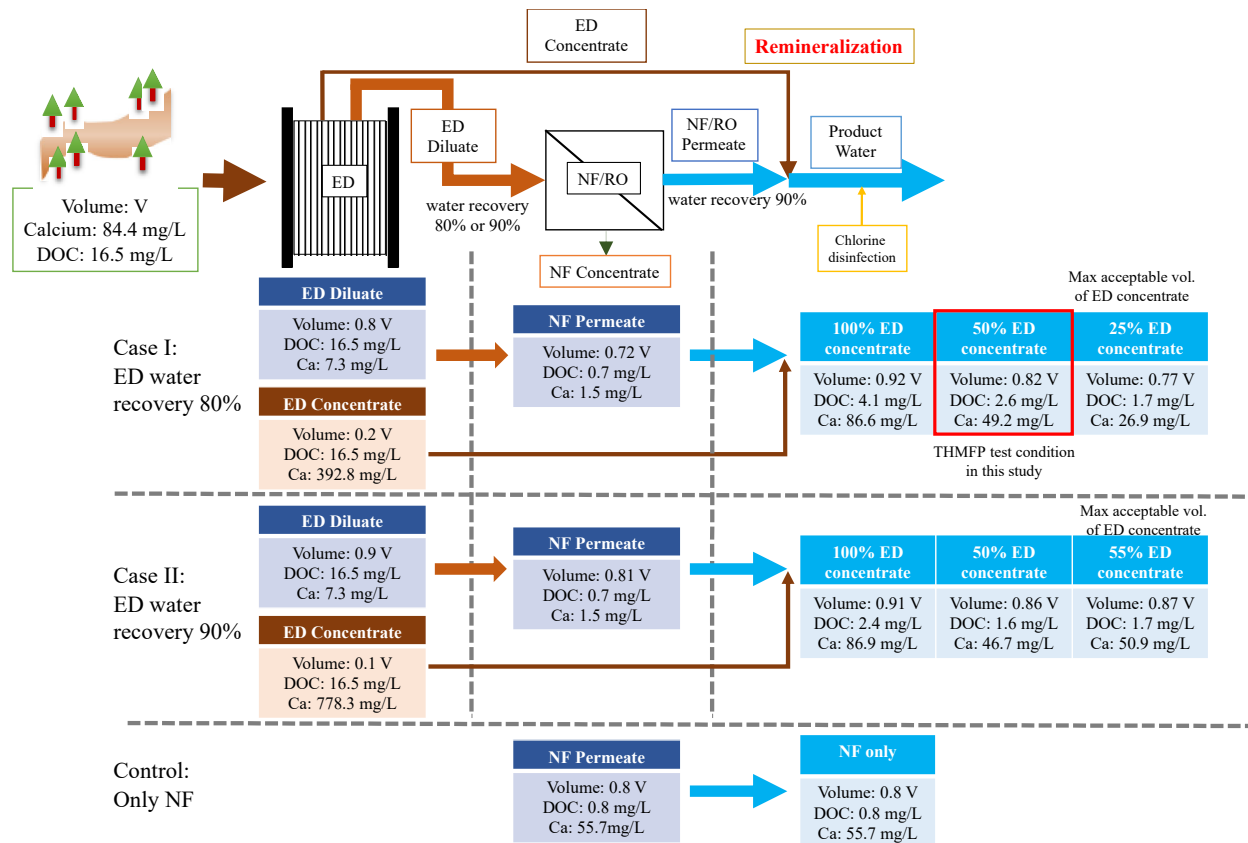
510 The two major advantages of the hybrid ED-NF system are the greater productivity of an
511 NF system and the potential to reduce DBP formation. The two raw waters from actual treatment
512 plants in Texas and Florida were put through the hybrid ED-NF system. For the TWN, ED was
513 operated at 80% recovery and 80% conductivity reduction, and the diluate was then applied to
514 the NF stage. The entire volume of the ED concentrate (20% of the original water) was then
515 mixed with the NF permeate; the water recovery from this system is intrinsically greater than
516 with NF alone because of the greater volume throughput prior to the need for membrane cleaning

517 (as shown in Figure 3) and the use of the entire ED concentrate. The trihalomethane formation
518 potential (THMFP) of TWN of this mixture was $76 \pm 3 \mu\text{g/L}$, just below $80.0 \mu\text{g/L}$, the
519 Maximum Contaminant Level (MCL) of total THMs regulated by US EPA.⁶⁹ The THMFP of
520 TWN after treatment by the existing enhanced coagulation process was $150 \pm 3 \mu\text{g/L}$, far
521 exceeding the MCL.

522 The Florida water, with its much higher concentrations of inorganic ions and NOM, is
523 more complicated. With 80% recovery and 80% conductivity reduction in ED, mixing the full
524 ED concentrate with the NF permeate would not yield sufficient NOM reduction because the ED
525 concentrate has the original NOM concentration. Even using only half of the concentrate yielded
526 a THMFP of $112 \pm 10 \mu\text{g/L}$, well in excess of the MCL; the results are shown as Case I (with
527 50% ED concentrate) in **Error! Reference source not found.** However, a major advantage of
528 the proposed hybrid system is that it affords far greater flexibility in achieving treatment goals. A
529 lower DOC and resulting THMFP could be achieved in this hybrid ED-NF system in three
530 different ways, either singly or in combination: reducing the percent of ED concentrate in the
531 final blend, achieving higher ED recovery, or choosing a different NF membrane. The latter
532 would likely change removal efficiencies of all constituents as well as the NF water recovery.

533 Our experimentation did not include investigating all of these possibilities, but combining
534 results we did investigate with reasonable assumptions leads to the values shown in Case II in
535 **Error! Reference source not found.** The primary difference from Case I is the higher recovery
536 from the ED process (90% rather than 80%). Using the measured DOC and TTHMFP values and
537 assuming that the TTHMFP is proportional to the DOC⁷⁰ resulted in the determination that the
538 final DOC after blending the NF permeate and a fraction of the ED concentrate needed to be \leq
539 1.7 mg/L to achieve a TTHMFP value below $80 \mu\text{g/L}$. For Case I with 80% ED recovery, that

540 value could be achieved by blending 25% of the ED concentrate with the NF permeate, thereby
541 achieving an estimated 77% overall recovery; in **Error! Reference source not found.**, these
542 results are shown in the far-right column for Case I. For Case II with 90% ED recovery, the
543 maximum DOC of 1.7 mg/L could be achieved by blending 55% of the ED concentrate with the
544 NF permeate, achieving an estimated 87% overall recovery; this result is shown on the far right
545 of Case II in **Error! Reference source not found.** This recovery exceeds the estimated 80%
546 recovery if NF was used as the sole treatment; although the DOC and THM values would be
547 higher with the hybrid ED-NF process, the water would comply with DBP regulations, the
548 recovery would be greater, and the need for NF cleaning would be reduced. More generally, the
549 hybrid ED-NF system would need to be optimized for specific waters and applications, but this
550 example showcases its potential for achieving treatment goals with high water recovery for
551 challenging waters.



552

553 Figure 6. The product water quality control examples of FWN in the ED-NF system. Water
 554 quality calculations are based on ED experimental results in Figure 2 and NF experimental
 555 results in Figure 3 and Table 2. We assume that no DOC mass loss occurs at the ED concentrate
 556 stream in this calculation and that TTHMFP is proportional to DOC.

557 **5 Conclusions**

558 This study evaluated a hybrid ED-NF membrane system to treat freshwater with
 559 moderate to high hardness and NOM concentrations. Compared to NF alone, the hybrid ED-NF
 560 system provides increased product water yield, increased removal of inorganic cations and NOM
 561 by NF, and reduced NF membrane fouling. Furthermore, some or all of the ED concentrate,
 562 which contains most of the original ions, can be added to the NF permeate as an efficient means
 563 of remineralization. ED pretreatment shows excellent ion separation and minimal NOM

564 separation, but natural waters with hydrophobic NOM and high NOM and calcium
565 concentrations require additional efforts to prevent NOM adsorption to the IEMs in the ED
566 concentrate. A reduction of NOM fouling on the NF membrane after ED pretreatment was
567 observed in all tested NOM sources, and that reduction is primarily caused by the lowered ionic
568 strength and, particularly, the lowered divalent cation concentration. Spectroscopic and resonant
569 scattering measurements near the calcium K-edge confirm a significant contribution of calcium-
570 carboxyl interactions to fouling during NF, and the fouling mechanisms were similar among
571 several NOM sources without and with ED pretreatment.

572 The water produced from the hybrid ED-NF system would offer greater protection
573 against health issues associated with DBP formation (resulting from the interaction of NOM and
574 chlorine-based disinfectants). But, the amount of ED concentrate for remineralization should be
575 carefully determined to avoid excessive DBP formation and, perhaps, minimize the presence of
576 other toxic components. The hybrid ED-NF system is a promising treatment option, with a niche
577 in the drinking water industry for treating waters with moderate to high hardness and NOM
578 concentrations in their supply. The hybrid system would be worthwhile if the increased water
579 production by NF, extended NF membrane lifetime, reduced chemical use for the membrane
580 cleaning, and substituted remineralization process by ED concentrate stream offset the cost of an
581 ED system. Moreover, the operational flexibility that allows the operator to control the final
582 water TDS and DOC concentration is a major advantage of the hybrid system. This hybrid ED-
583 NF system with its operational flexibility could also be applied to other water sources with
584 charged inorganic ions and neutral charge constituents that synergistically impact fouling of NF
585 membranes.

586 **Supporting Information**

587 The Supporting Information is available free of charge at <https://pubs.acs.org/doi/XXXX>.

- 588 • Details on preparation of natural organic matter and synthetic feed waters (Section 1 and
589 2); two fresh water quality data (Section 3); ED and NF experimental methods (Section 4
590 and 5); the Specific Energy Consumption Calculation at the ED process (Section 6);
591 properties of NF270 membrane (Section 7); normalized permeate water flux calculation
592 (Section 8); details on source water characterization using HP-SEC and nanoparticle
593 tracking analyses and results (Section 9); impact of different cations on NF membrane
594 NOM fouling (Section 10); and details on ATR-FTIR, XPS, Synchrotron techniques and
595 further discussion of results (Section 11 to 13) (PDF)

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